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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: May 30, 1979

Project Title: Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle

Project No: E-20-666

Project Director: Dr. F. G. Pohland

Sponsor: U. S. Environmental Protection Agency

Agreement Period: From 3/23/79 Until ~~3/22/81~~ 1/22/83 ~~9-22-82~~ ~~3/22/82~~ ~~9/22/81~~

Type Agreement: Grant No. R806498010

Amount: $61,500 (EPA)
10,500 (GIT E-20-320)
$72,000 Total

Reports Required: Quarterly Progress Reports; Final Report

Sponsor Contact Person (s):

Technical Matters

Mr. Dirk R. Brunner
Environmental Engineer
Municipal Environmental Research Lab
Environmental Protection Agency
Cincinnati, OH 45268

Contractual Matters
(thru OCA)

Mr. Frederick L. Meadows, Chief
Grants Operation Branch (PM-216)
Environmental Protection Agency
Washington, D. C. 20460

Defense Priority Rating: N/A

Assigned to: Civil Engineering (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director—EES
Accounting Office
Procurement Office
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Library, Technical Reports Section
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Project File (OCA)
Project Code (GTRI)
Other ______

EORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 4-14-87

oject No. E-20-666B School/XXX CE

cludes Subproject No.(s) N/A

oject Director(s) F.G. Pohland XXXXX /GIT

onsor U.S. Environmental Protection Agency

tle Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle

fective Completion Date: 1/22/83 (Performance) 1/22/83 (Reports)

ant/Contract Closeout Actions Remaining:

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [X] Closing Documents
- [X] Final Report of Inventions
- [X] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other ______

ontinues Project No. ______ Continued by Project No. ______

OPIES TO:

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Other Duane H.
Angela DuBose
Russ Embry

ORM OCA 69 285

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
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TELEPHONE:
(404) 894-2265

July 5, 1979

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498

Dear Dirk:

Included herewith is the first quarterly progress report on Project R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" covering the period March 23, 1979 through June 30, 1979. Because of the delayed receipt of official approval for funding of the project, we are somewhat behind the schedule initially proposed but hope to gain ground during the current project period.

We appreciate your interest and continued support of our leachate recycle efforts and are looking forward to a successful augmentation of previous results and progress. This effort, coupled with our other cell studies, should strengthen the case for implementation on a larger scale. We are seeking operational data on such large scale installations, and would appreciate receiving information on any sites you may be familiar with if and when it becomes available.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

Enclosure
FGP:jp
cc: Dr. M. T. Suidan

Quarterly Progress Report No. 1
"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498010
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
March 23, 1979-June 30, 1979

With the final approval of support for initiation of the research studies on the fate of heavy metals in landfills with leachate recycle, this report period was devoted to the construction of the lysimeter-type landfill columns and the installation of operational appurtenances. A new platform has been constructed and the four 3-foot diameter, corrugated steel containment columns have been erected and secured. The foundation for and placement of the leachate reservoirs has also been completed and two equipment sheds have been assembled to house these sumps, the recycle pumps, and other instrumentation as well as to provide insulation and security.

Present effort is being placed on the acquisition and installation of the recycle lines, valves and collection and distribution manifolds. In addition, sensor probes are being placed to provide records of temperature and ORP prior to placement of the final insulation. Sources of heavy metals are being sought locally, concentrating on the metal plating and finishing industry. A source of domestic-type municipal refuse has been located and arrangements are being made for delivery to the research site on schedule.

Preliminary investigations on the requisite mixing of the heavy metals and fixing materials (fly ash, kaolin and sawdust) have also been initiated to ascertain handling characteristics, leaching properties, and relative sorption-desorption characteristics. These investigations are being conducted in small laboratory columns employing anticipated quantities of admix materials. Results of these studies will be used as guidance in preparing the heavy metal-admix compositions for the experimental lysimeter-type columns.

It is anticipated that the construction and instrumenting of the four simulated landfill columns will be completed and that the refuse-heavy metal mixtures will be placed during the next report period. To expedite the initiation of leaching, the columns will be brought to field capacity artificially with tap water. This experimental expediency will be similar to that used during the original recycle studies and will hasten receipt of meaningful experimental data.

Frederick G. Pohland
Project Director

E-20-664

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TELEPHONE:
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October 17, 1979

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"

Dear Dirk:

Enclosed herewith is the second quarterly progress report on the subject research project covering the period July 1, 1979 through September 30, 1979. Your perusal of the report will indicate that we have completed construction and filling of the columns, have brought them to apparent field capacity, and have initiated recycle. We are presently obtaining analyses of initial samples which will be included in more detail in the report of the next project phase.

I appreciate your continued interest and support of our research efforts and would welcome receipt of complementary information and results from other studies to which you have access.

It was pleasant meeting with you recently in Berlin. Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP:jp
Enclosures
cc: Dr. J. E. Fitzgerald
Ms. Pat Davis

xc: Rodgers /w/rpts

Quarterly Progress Report No. 2
"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
July 1, 1979-September 30, 1979

During this project phase, construction and instrumentation of the four simulated landfill columns was completed sufficiently to permit filling of the columns with the municipal refuse and metal sludge. The municipal refuse was delivered in a 30 cu. yd. compactor vehicle from a residential area in DeKalb County, Georgia. Separation and analysis of about a quarter of the refuse yielded the following fractional quantities, moisture and volatile contents.

Fraction	%, wet weight	% moisture	% volatile
Paper	53.0	11.6	87.5
Plastics, Rubber, Leather, Textiles	8.4	2.5	98.6
Diapers	2.9	34.3	98.2
Glass	13.7	-	-
Metals	5.9	-	-
Food Wastes	6.2	75.4	91.9
Garden Debris	1.8	62.8	92.4
Wood	2.0	-	-
Residues	6.1	45.1	89.6

A total of 880 pounds (400 Kg) of refuse was placed in each column above a gravel/pipe underdrain system and compacted manually during placement. Column 1 was designated the control and contained only refuse and sawdust essentially equivalent to the amount added to each of the other columns ($\sim$82 pounds). Columns 2, 3 and 4 received, in addition to the refuse and sawdust, 74, 145 and 298 pounds of metal plating sludge, respectively. The sawdust or sludge/sawdust mixtures were added in increments throughout the filling process to distribute the materials through the depth of the columns. Each column was then covered with 1000 pounds of soil above the refuse and gravel/pipe redistribution system.

The metal plating sludge was obtained at a local metal finishing operation and was produced in a semi-solid form by pretreatment at the plant. Sawdust was added to this sludge to transform it to a more manageable consistency and to simulate probable admix procedures used at an actual landfill site. Analyses are being completed on the sludge to record total quantities of metals and other constituents added to each column. These results will be reported in detail in the next progress report and are anticipated to indicate Pb, Zn, Cd, Cu and Cr concentrations available for possible leaching as leachate recycle proceeds.

The addition of the refuse/sawdust and refuse/sludge/sawdust mixtures, coupled with the gravel and soil cover and the eventual addition of moisture, has caused some compression to occur. This compression is continuing with the onset of leachate collection and recycle and will eventually yield an initial density of the contents of each column. Leachate collection was incurred by addition of tap water to each column until leaching commenced. Depending upon the moisture content in each column, varying quantities of tap water with rainfall were introduced to allow for a similarity of total leachate volume discharged from each column. This process of attaining apparent field capacity is continuing and records of quantities of leachate collected and recycled daily as well as analyses on initial leachate samples from each column are being developed. Again, more detailed results will be presented in the progress report for the next project phase.

The next project phase will also be devoted to completion of construction and instrumentation of the columns including insulation for temperature modification and automation of some of the routine analytical parameters. Particular attention will also be given to the acquisition of data indicative of ion mobilization and possible effects on establishment of normal biological stabilization patterns.

Frederick G. Pohland
Professor of Civil Engineering

E-20-666

Quarterly Progress Reports No. 3 and 4
"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
October 1, 1979 - March 31, 1980

During this phase of the project, leachate recycle was continued in an attempt to normalize the concentration of leachate constituents extractable from each of the simulated landfill columns. Superimposed upon these results were the dilution effects resulting from continuing influx of rainfall which has been significant during the latter portion of this report period. As quantities of leachate accumulated, some leaking was also detected around the base of the columns, particularly column 3, which has not been completely resolved to date. This leaking has interfered with the initiation of a routine recycle schedule which has been automated to allow for a daily turnover of the leachate in each column. Efforts are continuing in an attempt to provide for additional sealing of all columns to preclude any future loss of leachate.

Prior to the time that leaking problems developed in the columns, initial analytical data were accumulated on the leachate from the four simulated landfill columns. Selected data are compared in Table 1 for samples collected after initial addition of tap water (September 14, 1979) and after about four months of operation (February 24, 1980). Of interest here has been the apparent establishment of reducing conditions in the columns and corresponding reductions in pollutant concentrations as a consequence of both dilution and internal biological and physical-chemical interactions. The total addition of tap water to each column was 210 liters; on February 24, 1980, an additional 410 liters of rainfall had been recorded for each column.

Notwithstanding the dilution effect, biochemical activity has probably been subdued somewhat by correspondingly low temperatures experienced at the time of the second (4-month) sample, i.e., about $4^{\circ}C$ despite the addition of insulation around the exterior of each column. Therefore, although freezing conditions did not occur, temperatures were decreased sufficiently to retard rapid biological degradation and/or removal of available organics in the leachates.

Some trend is noticeable with respect to constituents in the leachates from the four columns. It is likely that the column receiving no metal sludge was more biologically active sooner and had opportunity to display greater removals of organic pollutants as well as the metals of concern. An abundance of sulfate from the industrial metal sludge and its reaction to yield sulfides and moderate the ORP probably led to precipitation of heavy metals in the control as well as in the other three columns. Excess amounts of metals in these latter columns would be expected to rapidly use sulfides present and continue to do so as long as metals remain unprecipitated and sulfide can continue to be generated. The rate of reduction of sulfates to sulfides and their availability for reaction therefore has significance with respect to both the immobilization of heavy metals and their effect on inherent microbial activity.

It is too early to determine metal effects on biological activity although the initial data (Table 1) would suggest some inhibition since higher organic concentrations (COD and TVA) existed in the leachates from the columns receiving metal sludge. More recent data tend to confirm this but temperatures have not stabilized at higher levels yet to eliminate that retarding influence. As temperatures increase, adverse temperature effects will be minimized and biological activity will be expected to accelerate at least where inhibition by metals is not operative. In addition, it is possible that as the residual metal concentrations are diluted by rainfall, acceptable levels will be reached at which time opportunities for biological activity would be expected to be enhanced.

Table 2 records the characteristics of the metal sludge added to the test columns. As indicated, zinc is the predominant heavy metal which is also reflected by comparative metal concentrations in the respective leachate samples. Just how much of these metals will be leachable from the columns remains to be determined; the return to near neutral conditions consequenced by the lime content of the metal sludge would tend to make the metals less mobile. The overall fate and reactivity of the metals in the columns and leachate will continue to be a prime focus of attention in subsequent periods of the investigation. Precipitation and/or filtration with recycle will remain the most probable attenuation mechanism either naturally or with the possible external mediation of ORP/sulfide conditions.

Most recent analytical data (March 10, 1980) from the leachate of the four columns with respect to those parameters reflecting the relative mobility of metals indicate a pH of 6.42, 6.86, 6.77 and 6.55; an ORP of -65, -75, -85 and -65 mv; and, zinc concentrations of 0.45, 50, 50 and 188 mg/l in the four columns, respectively. Sulfide concentrations were very low, < 1.0 mg/l, and other metals were almost nondetectable. Additional decreases in COD and TVA seem to have been consequenced primarily by the diluting effects of rainfall. Attempts are presently being directed toward definition of this effect and the causes for possible differences between the leachate generated by the four columns. More detailed results on the experimental study will be included in the progress report of the next project period.

A portion of these results were presented at the Sixth Annual Research Symposium on Treatment and Disposal of Hazardous Waste held in Chicago in March 1980.

Frederick G. Pohland
Professor of Civil Engineering

TABLE 1. COMPARISON OF SELECTED LEACHATE CHARACTERISTICS FROM LYSIMETER INVESTIGATIONS OF CODISPOSAL OF RESIDENTIAL-TYPE SOLID WASTES WITH INDUSTRIAL WASTE UNDER THE INFLUENCE OF LEACHATE RECYCLE

	ANALYSES							
	COLUMN 1		COLUMN 2		COLUMN 3		COLUMN 4	
PARAMETER	INITIAL	4-MONTH	INITIAL	4-MONTH	INITIAL	4-MONTH	INITIAL	4-MONTH
pH	5.68	7.01	5.45	6.83	6.08	7.05	6.17	6.58
COD, mg/l	11,740	2,090	20,830	6,220	13,450	6,470	13,830	8,560
TVA, mg/l CH_3COOH	989	336	1,320	542	874	754	1,220	640
ORP, mv E_c	-100	-90	-80	-40	-90	-45	-80	-30
SULFATE, mg/l	34	5	218	250	104	230	109	120
SULFIDE, mg/l	1.2	0.07	0.03	0.004	0.03	0.004	0.03	0.007
METALS, mg/l								
ZINC	3	0.62	500	185	205	75	390	162
CHROMIUM	0.05	ND	0.28	TRACE	0.20	TRACE	0.12	TRACE
NICKEL	0.10	TRACE	1.1	0.68	0.82	0.38	1.2	0.56
CADMIUM	ND	ND	1.7	0.9	1.1	1.0	2.0	1.5
IRON	25	12	88	13	68	40	62	21

COLUMN 1: CONTROL WITHOUT METAL SLUDGE

COLUMN 2: TEST UNIT WITH 33.6 KG OF METAL SLUDGE

COLUMN 3: TEST UNIT WITH 65.8 KG OF METAL SLUDGE

COLUMN 4: TEST UNIT WITH 135.2 KG OF METAL SLUDGE

TABLE 2. CHARACTERISTICS OF METAL SLUDGE USED IN LYSIMETER INVESTIGATIONS WITH RESIDENTIAL-TYPE SOLID WASTES CODISPOSAL AND LEACHATE RECYCLE

Parameter	Analysis
Moisture Content, %	84.7
Volatile Solids, %	24.6
Zinc, mg/kg dry	317,000
Chromium, mg/kg dry	21,000
Nickel, mg/kg dry	400
Cadmium, mg/kg dry	13,100
Copper, mg/kg dry	185
Iron, mg/kg dry	94,000

Note: Metals determined after acid digestion.

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
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July 15, 1980

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization with Leachate Recycle" (E-20-666)

Dear Dirk:

Enclosed herewith is the fifth quarterly progress report on the subject research covering the period April 1, 1980, through June 30, 1980. The data summary includes illustrations of selected data through May 10, 1980 (Day 240) with additional commentary on more recent results. The figures are presented for inspection in draft form but will be polished later when additional data are accumulated.

In spite of some difficulties in sealing the columns, we are now obtaining some interesting results which suggest that a municipal landfill operated with leachate collection and recycle can attenuate and contain otherwise hazardous materials. To that extent, the research is on schedule with our original expectations, and we look forward to receipt of additional confirmation of this premise.

We appreciate your continued interest and support of our research efforts.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP/kcb

Enclosure

cc: Dr. J. E. Fitzgerald
Ms. Pat Davis

Quarterly Progress Report No. 5
"Fate of Heavy Metals During Landfill Stabilization of
Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
April 1, 1980 - June 30, 1980

During this phase of the project, leachate recycle was continued in each simulated landfill column at frequencies of one liquid recycle per day. This translates to about five minutes pumping time followed by two to three hours to drain the free liquid from the columns. The present total accumulations of leachate in the column are about 50 to 60 gallons each except for Column 3 which has been subject to some leaking problems where about 30 gallons of leachate remain. Accordingly, discounting Column 3, about 175 to 185 gallons of rainfall (including the 50 gallons of tap water initially added) have been contained within the columns or lost through evaporation. Since leaking of Column 3 occurred after the constituent concentrations in the leachate during recycle had essentially stabilized, concentrations of inorganic species in the leachates from the columns were relatively similar and no attempt was therefore made to replace the lost volume of leachate in Column 3.

Regarding the leachate constituents, selected data are presented graphically in Figures 1-6. Figures 1-3 illustrate the initially high concentrations of metals (Zn, Ni and Cd) in the leachate from the three test columns. These concentrations tended to persist for some time after which they decreased as a consequence of dilution and reaction within the landfill mass. Initial variations in concentrations from each test column were due to the initial amount of metal sludge added and the time required to reach some "steady state" concentration determined by the extent of distribution of flow and reactivity within each column. About 110 days (from September 14, 1979 to January 1, 1980) were required to reduce metal concentrations to relatively low but lingering values. Through 240 days (May 10, 1980), these concentrations in the test columns were slowly diminished further and subsequent data have indicated a continuation of this trend.

The apparent mobility of the metal constituents in the leachate is considered to be a function of the environmental conditions as characterized by such parameters as pH, ORP, sulfide-sulfate equilibrium, and possibly temperature. The low pH experienced during the initial phase of the investigations (Figure 4) and up to January 1, 1980 in each column would enhance the mobility of metals. An increase in pH together with the establishment of reducing conditions and the availability of sulfides would tend to further augment removal of metals.

During the period after the increase in pH occurred in the test units, ORP values have been ranging within about -65 to -100 mv E_c and sulfides have always been available, usually in concentration between 0.3 and 1.0 mg/l. The excess sulfate in the metal plating sludge added to the test columns tends to act as a reservoir of sulfur species, thus allowing for further interaction with and attenuation of metals by precipitation and filtration during leachate recycle. More recently, ORP levels have become even more negative (~-300mv) which enhances removal of the metals and also the potential for biological stabilization to even a greater extent. Moreover, there is some recent evidence that the sulfide level is rising in the leachate which is consistent with the disappearance of high metal concentrations, a lower ORP and a potentially more active biological system in the test columns. This activity would be catalyzed by the higher ambient temperatures now being experienced (>35°C).

Concerning the behavior and fate of the organic constituents transferred to the leachate from each column originally, the control column (Column 1) tended to decrease more rapidly in concentration than the other columns (Figure 5). This may have been due to the absence of inhibition by metals in this column so that biological stabilization could proceed unhindered. The other columns apparently lagged behind Column 1, although some decrease in concentration occurred but mostly after the pH had risen and become more favorable (January 1, 1980). Moreover, it is unlikely that the reductions noted were a sole consequence of dilution, since chloride analysis (Figure 6) did not demonstrate as radical a decrease in concentration with increasing accumulation of leachate.

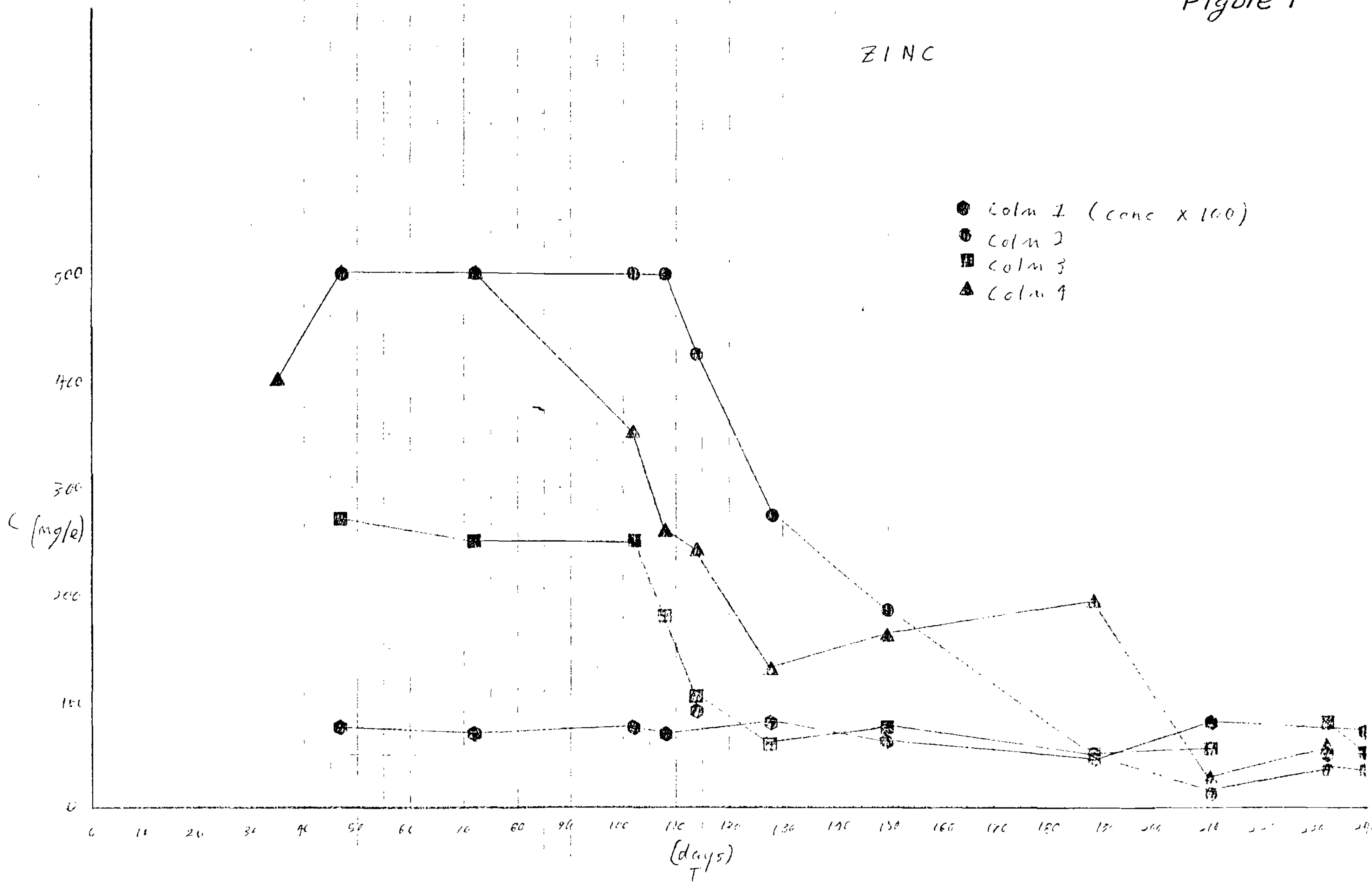
The difference between the control column and test columns in terms of COD removal suggests an inhibition of normal biological activity by the metal sludge at least until metal concentrations in the leachates had been decreased to low levels (Figures 1-3). This premise has been further substantiated by more recent COD analyses; Column 1 COD has remained consistently low, whereas the COD of Columns 2, 3 and 4 have risen to 4721, 8139 and 4856, respectively, at the end of June 1980. This observation is consistent with the more favorable environmental conditions, i.e., higher pH, lower ORP, low metals and high temperature enhance biological conversion of complex organic matter to simpler intermediates and end products. In addition, volatile acid analyses have indicated the veritable absence of the lower fatty acids in Column 1 leachate and increasing concentrations in each of the Column 2, 3 and 4 leachates to >1500 mg/l as acetic acid at the end of June 1980.

It is anticipated that the process of conversion of organic material will continue with eventual decrease and/or removal of available organic constituents in the leachate as methane fermentation becomes established within the test columns. Present emphasis is being placed on close monitoring of these changes in leachate quality nutrients. This latter effort, along with TIC and TOC analyses, will permit a determination of the nature of effluent COD concentrations and whether nutrients such as nitrogen or phosphorus become limiting. Data to date suggest that an abundance of nitrogen is available to support active biological metabolism but that phosphorus may eventually become limiting. Results of these analyses will be included in the next progress report.

A portion of the results included herein will be prepared for presentation at the 49th Annual Conference of the Georgia Water Pollution Control Association scheduled for Jekyll Island, Georgia, August 24-27, 1980.

Frederick G. Pohland
Project Director

Figure 1


ZINC
Colm 1 (conc x 100)
Colm 2
Colm 3
Colm 4
C (mg/l)
500
400
300
200
100
0
(days)
T

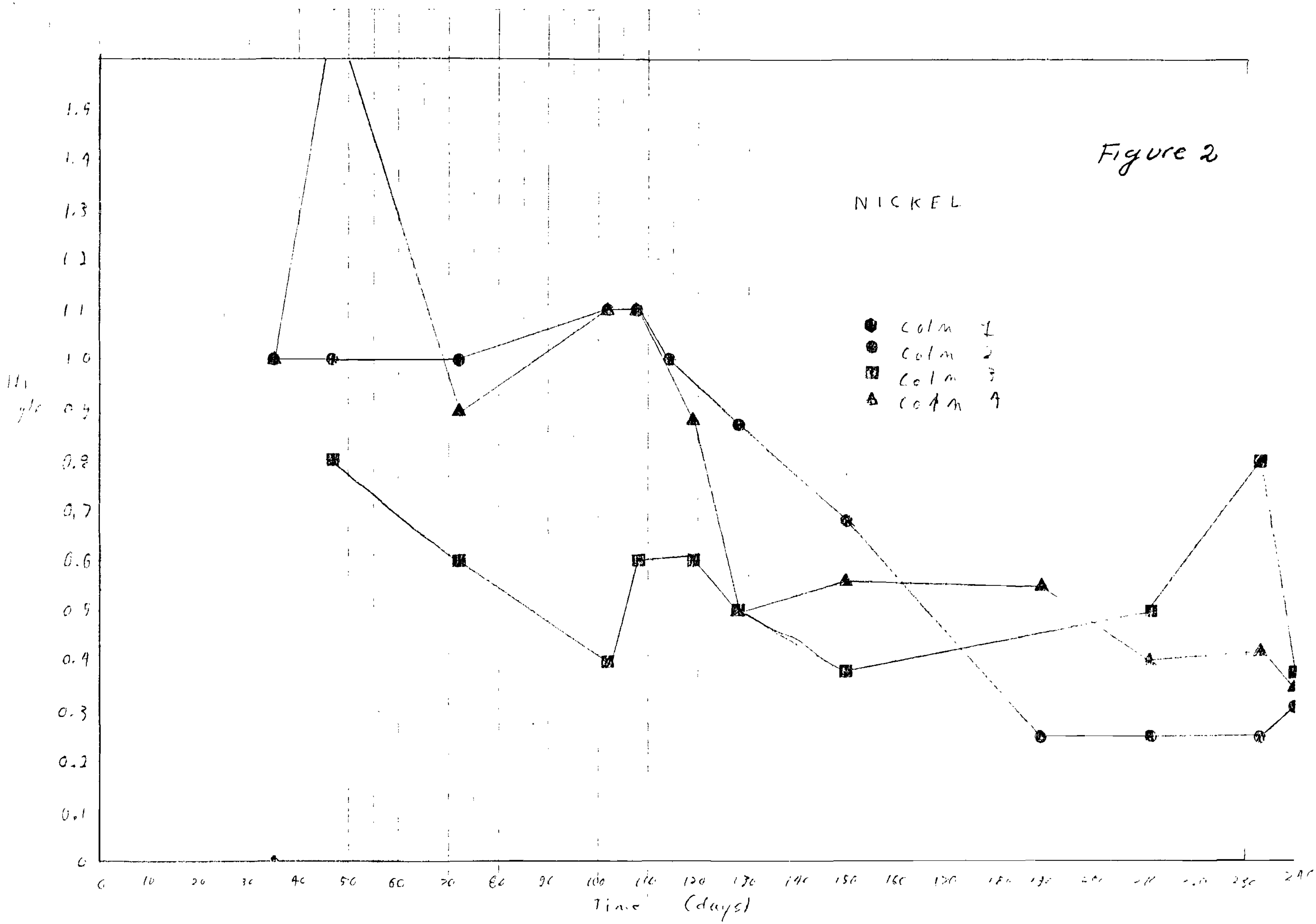
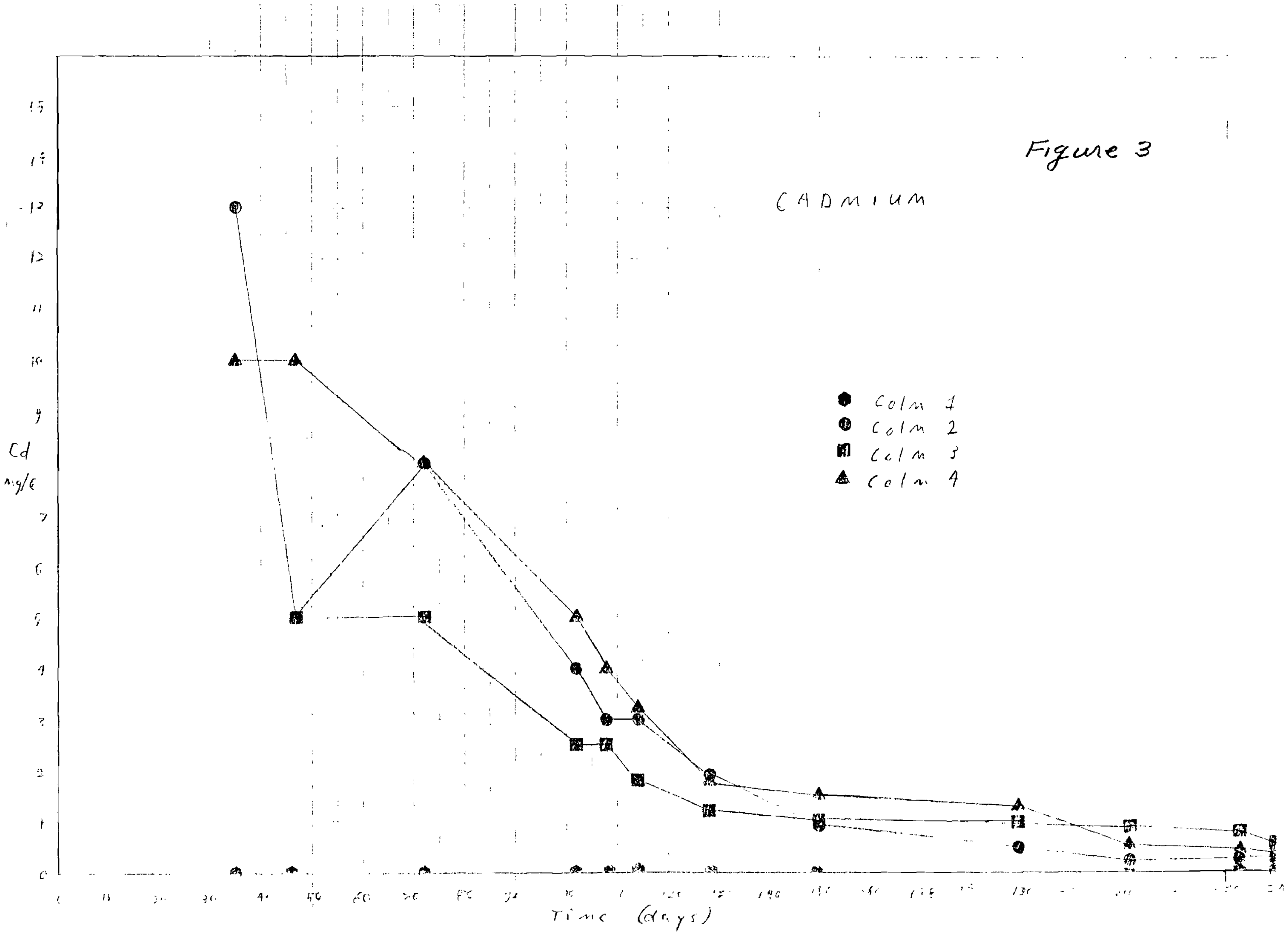


Figure 2
NICKEL
Colm 1
Colm 2
Colm 3
Colm 4
Time (days)

Figure 3



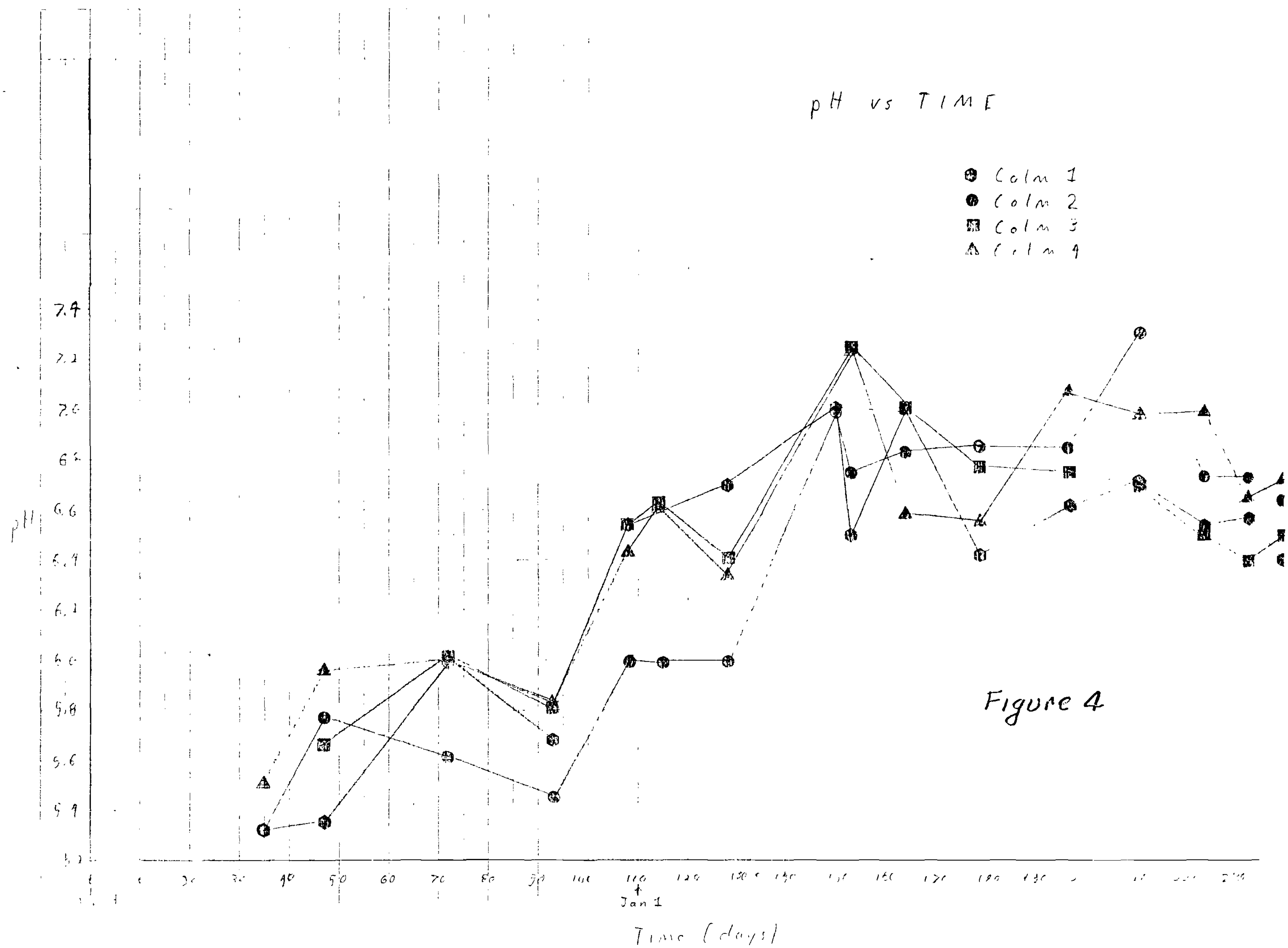
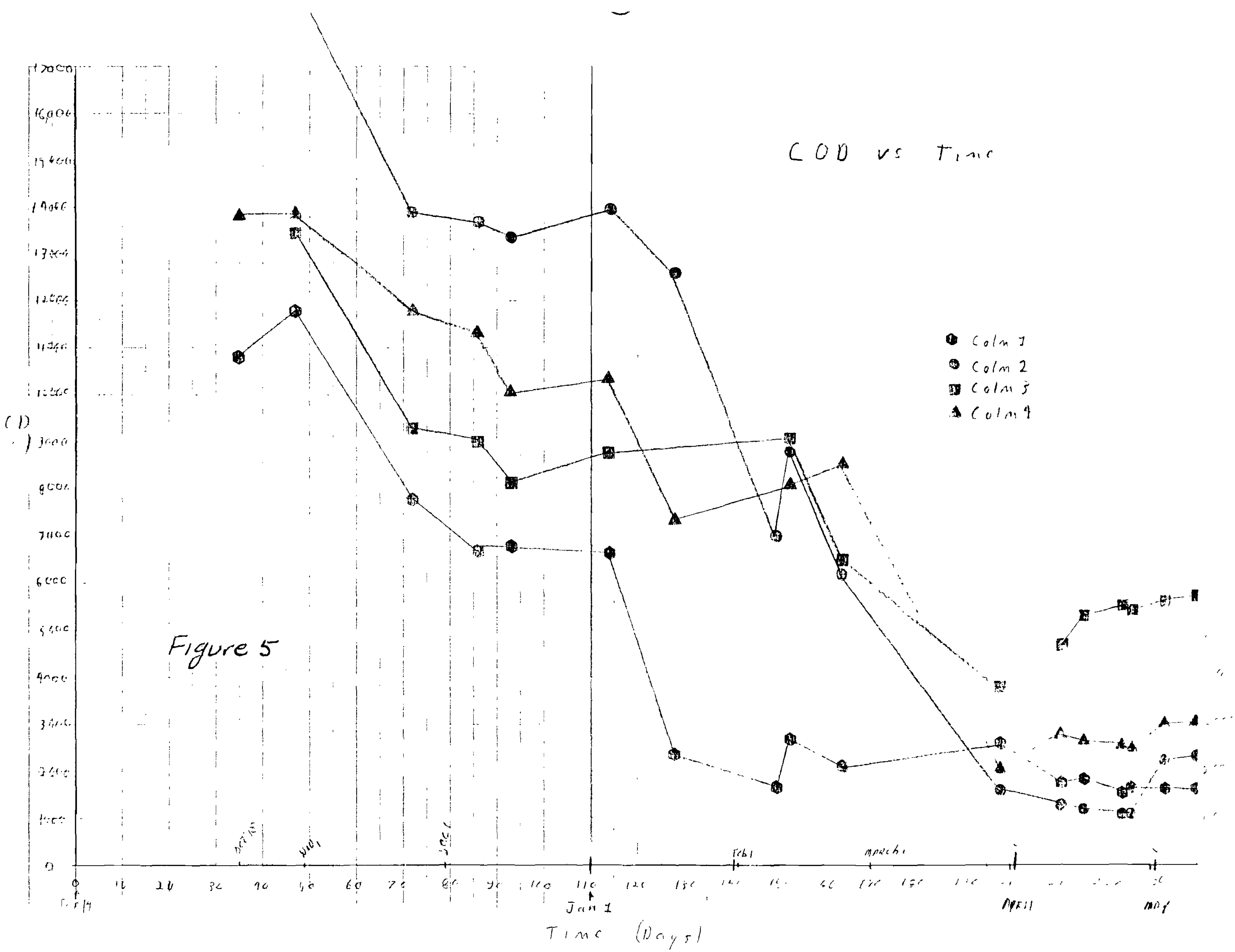


Figure 4



COD vs Time
Colm 1
Colm 2
Colm 3
Colm 4
Figure 5
Jan 1
Time (Days)
April
May

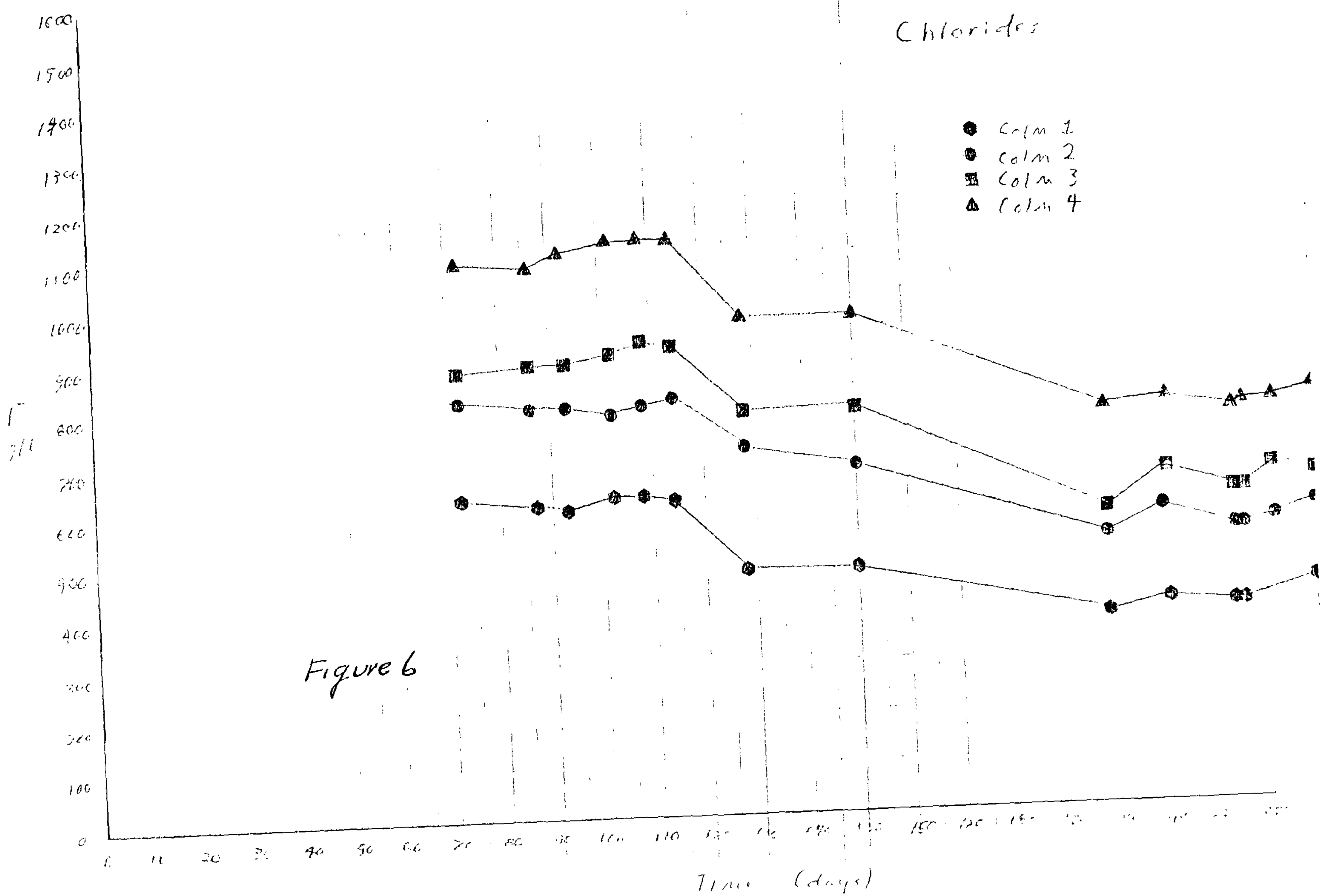


Figure 6

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(404) 894- 226.

October 9, 1980

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals
During Landfill Stabilization
of Solid Waste ~~Materials with~~
Leachate Recycle" (E-20-666) pcb

Dear Dirk:

Enclosed herewith is the sixth quarterly progress report on the subject research covering the period July 1, 1980 through September 30, 1980. The data summary in the enclosed figures extends some of the information presented in the previous quarterly report into October 1980. These figures are again presented in draft form and will be polished later for presentation at the Seventh Annual Research Symposium scheduled for March 1981.

Your perusal of the report will indicate that the quantities of leachate available for recycle have diminished considerably. This has no doubt been consequenced by an exceedingly dry and hot summer period and possibly by a continuing saturation of the column contents. However, this apparently has not caused unusual changes in the indicator parameters and we would expect that additional leachate will become available when local rainfall begins to increase.

As mentioned in our recent telephone conversation, I would request that you send me some of the typing guides for preparation of a draft project report so that previous project results can be reported. If available, I would also appreciate receiving a copy of the Proceedings of the 5th Annual Research Symposium, Municipal Solid Waste: Land Disposal, EPA-600/9-79-023a, August 1979. My copy has been misplaced and I need to reference some of the work contained therein.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP:jp
Enclosure
cc: Dr. J. E. Fitzgerald, CE
Ms. Faith Costello, GTRI

PS. Back in July 1980, I submitted forms for reappointment as a consultant to the Solid and Hazardous Waste Research Division via a request from Ron Hill per Norb Schomacher. I would appreciate being informed whether this reappointment has materialized.

G.

Quarterly Progress Report No. 6
"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
July 1, 1980 - September 30, 1980

During this phase of the project, leachate recycle was continued in each simulated landfill column at a frequency of one liquid recycle per day. Although the actual pumping time to recycle accumulated leachate has been short (~5 minutes), the time required for the leachate to flow through each column has varied from about 3 to 4 hours for Column 4 to about 8 hours for the other columns. Indeed, leachate accumulation ceased in Column 2 in early August 1980 and since that time, no leachate recycle in that column has been provided.

Since the last report period, the quantity of leachate available for recycle in the four experimental columns has diminished to about 7, 0, 5 and 30 gallons in Columns 1, 2, 3 and 4, respectively. This decrease in available leachate has been consequenced by a removal of some quantity required for sampling but also the fact that little rainfall and very hot and dry conditions have prevailed during this experimental period. Moreover, the disappearance of measurable leachate from Column 2 suggests the possibility that additional moisture is being accumulated in that column and perhaps also in the others. It is possible that complete saturation of the total contents of the columns has not yet been attained and/or that moisture is being replaced to accommodate that lost through drying. The cause of this occurrence should be resolved as more rainfall becomes available.

Regarding the leachate constituents, additional chloride data (Figure 1) indicate not much change in concentration since that previously reported and if anything, a gradual increase. This would be consistent with a decrease in the total quantity of leachate available from each column. A similar behavior was noted for COD analyses, however, an increase in Column 1 did not materialize which rather suggests that as warmer weather prevailed and metal concentrations became low, release of organics from the test columns was enhanced. A more thorough saturation of the column contents with recycled leachate would also encourage additional release of organic constituents. The decrease in COD concentrations toward the end of this report period could also indicate a biological conversion as was already completed in Column 1 where metal toxicity was absent.

The metal concentrations detected in the leachate samples also remained at the low levels reported previously. Current levels are now considered to exert an inhibitory influence so that it is anticipated that available COD will continue to be biologically removed as it either not exists in the leachate or continues to be extracted from the column contents. The presence of volatile acids in the leachate further suggests a continuing biological activity commensurate with their availability and as they are converted, additional reduction in COD should be observed.

Recent BOD_5 analyses indicate that the $COD:BOD_5$ ratio in the three test columns is about 0.5; BOD_5 residual in Column 1 has stabilized at about 50-60 mg/l. Respirometer studies are currently being conducted to determine if possible nutrient deficiencies and/or inhibition exist although, at least for nitrogen and phosphorus in the former case, sufficient nutrients as N or P appears to be available. Figures 3, 4 and 5 indicate current levels of phosphorus and nitrogen as measured in the leachate samples from the experimental columns.

The pH and ORP continue in ranges favorable for biological conversion of leachate constituents (Figures 6 and 7). Measurement of ORP continues to be rather challenging both due to the relatively small quantity of leachate available and the difficulty of limiting exposure of samples to the atmosphere during sampling and analysis. However, negative values have prevailed which are conducive to conversion of organic intermediates to CO_2 and CH_4. The changes in ORP from sampling period to sampling period also are reflected similarly in the sulfide analyses which will be discussed in more detail in the next progress report.

A portion of the results included herein was presented at the 49th Annual Conference of the Georgia Water Pollution Control Association in August 1980. A more current and complete presentation is being prepared for the Seventh Annual EPA Research Symposium scheduled for Philadelphia in March 1981.

Frederick G. Pohland
Project Director

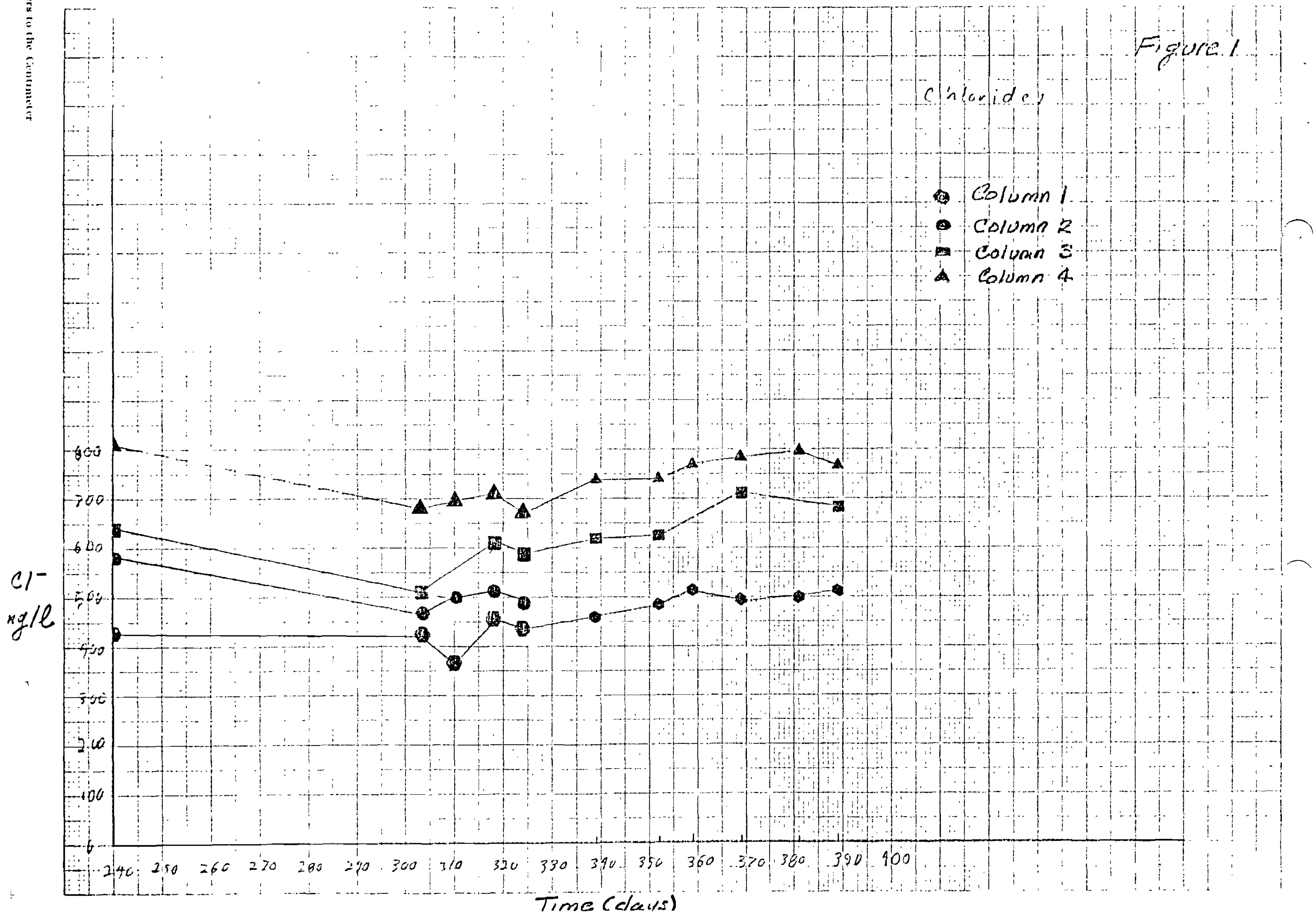
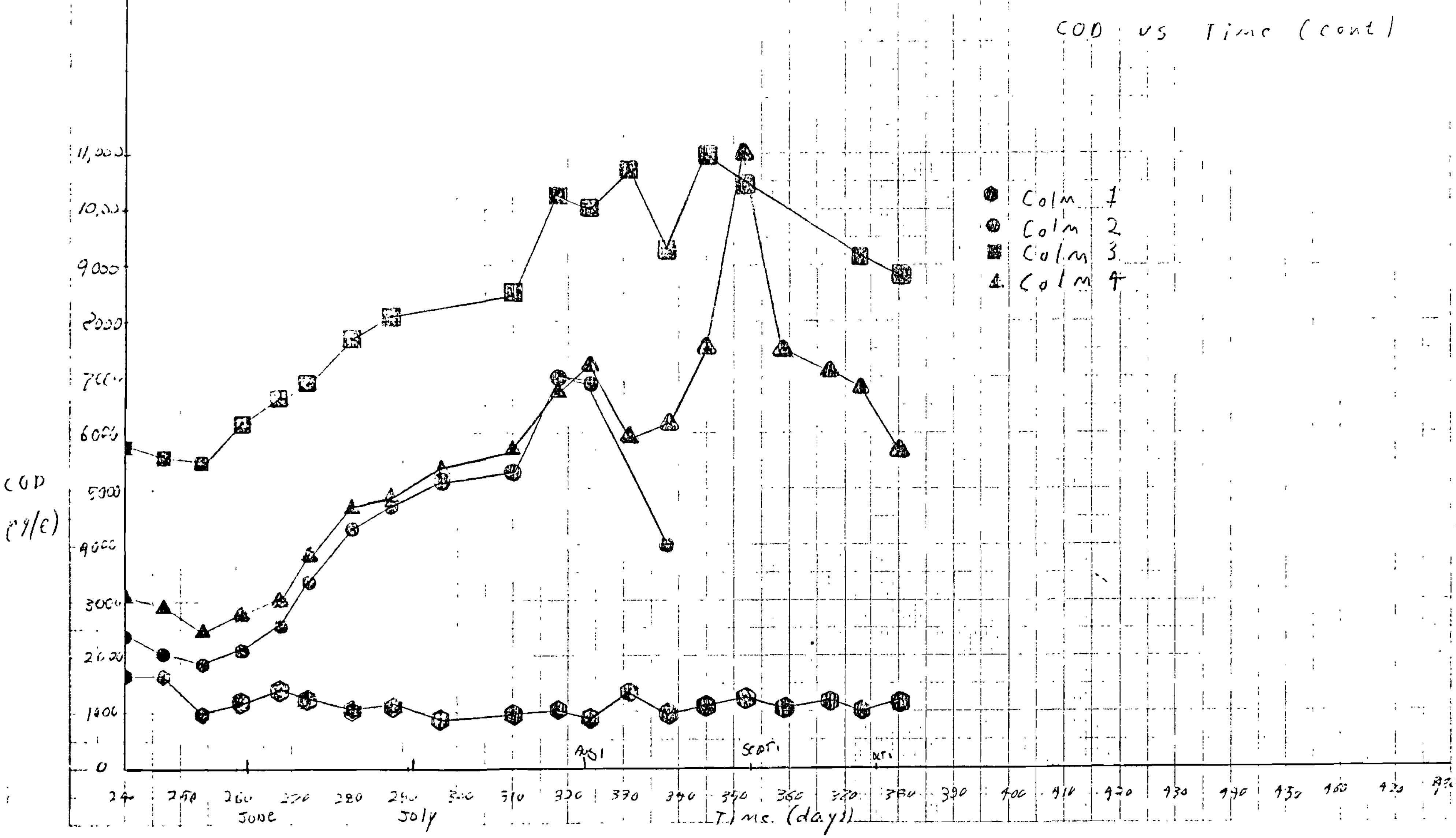


Figure 1
Chloride
Column 1
Column 2
Column 3
Column 4
Cl⁻
mg/l
800
700
600
500
400
300
200
100
0
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
Time (days)

Figure 2



COD vs Time (cont)
Colm 1
Colm 2
Colm 3
Colm 4
COD
(mg/l)
Time (days)
June
July
Aug
Sept
Oct

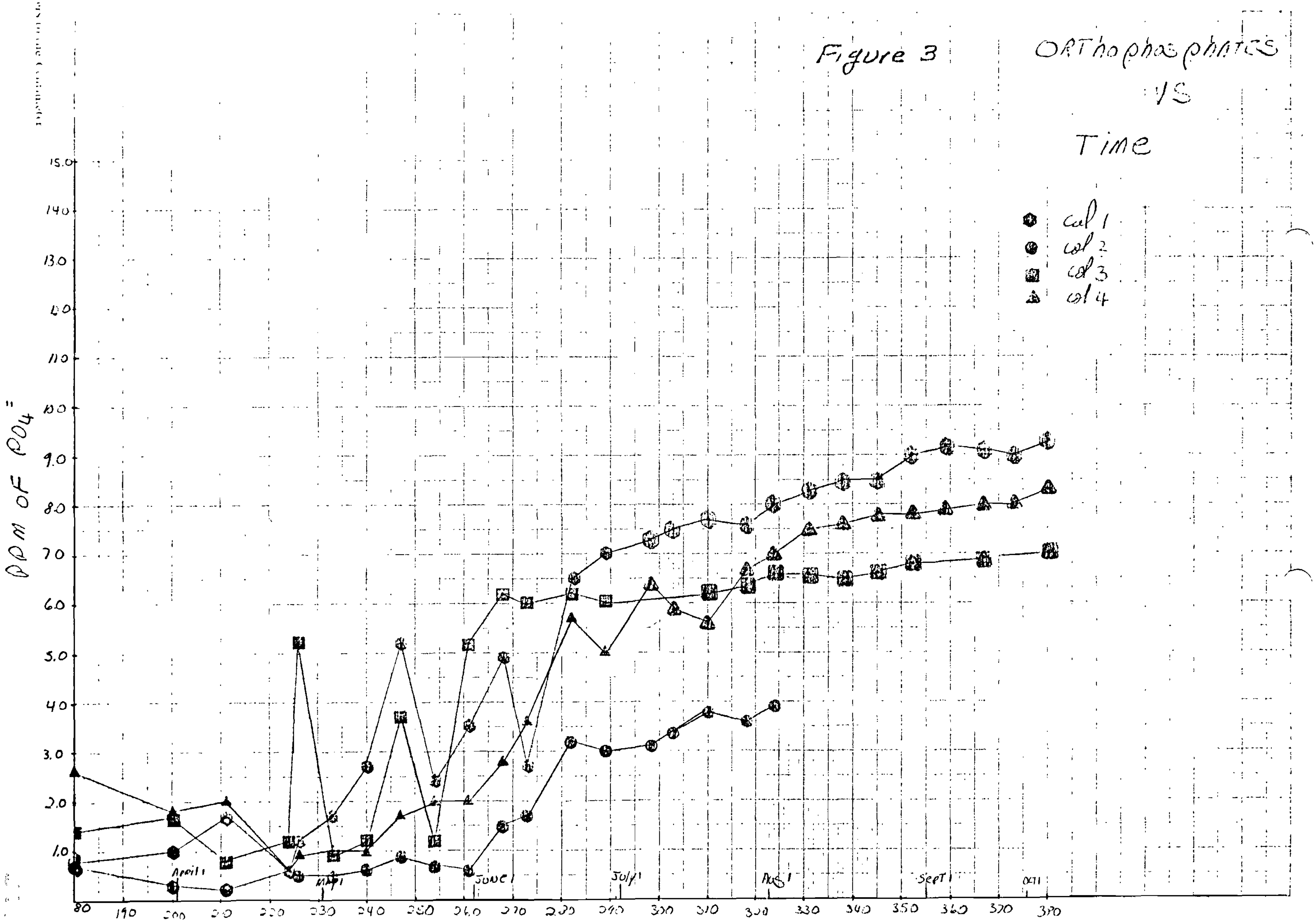


Figure 3
ORThophosphates VS Time
col 1
col 2
col 3
col 4
PPM OF PO4"
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
April 1
May 1
June 1
July 1
Aug 1
Sept 1
Oct 1
180
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380

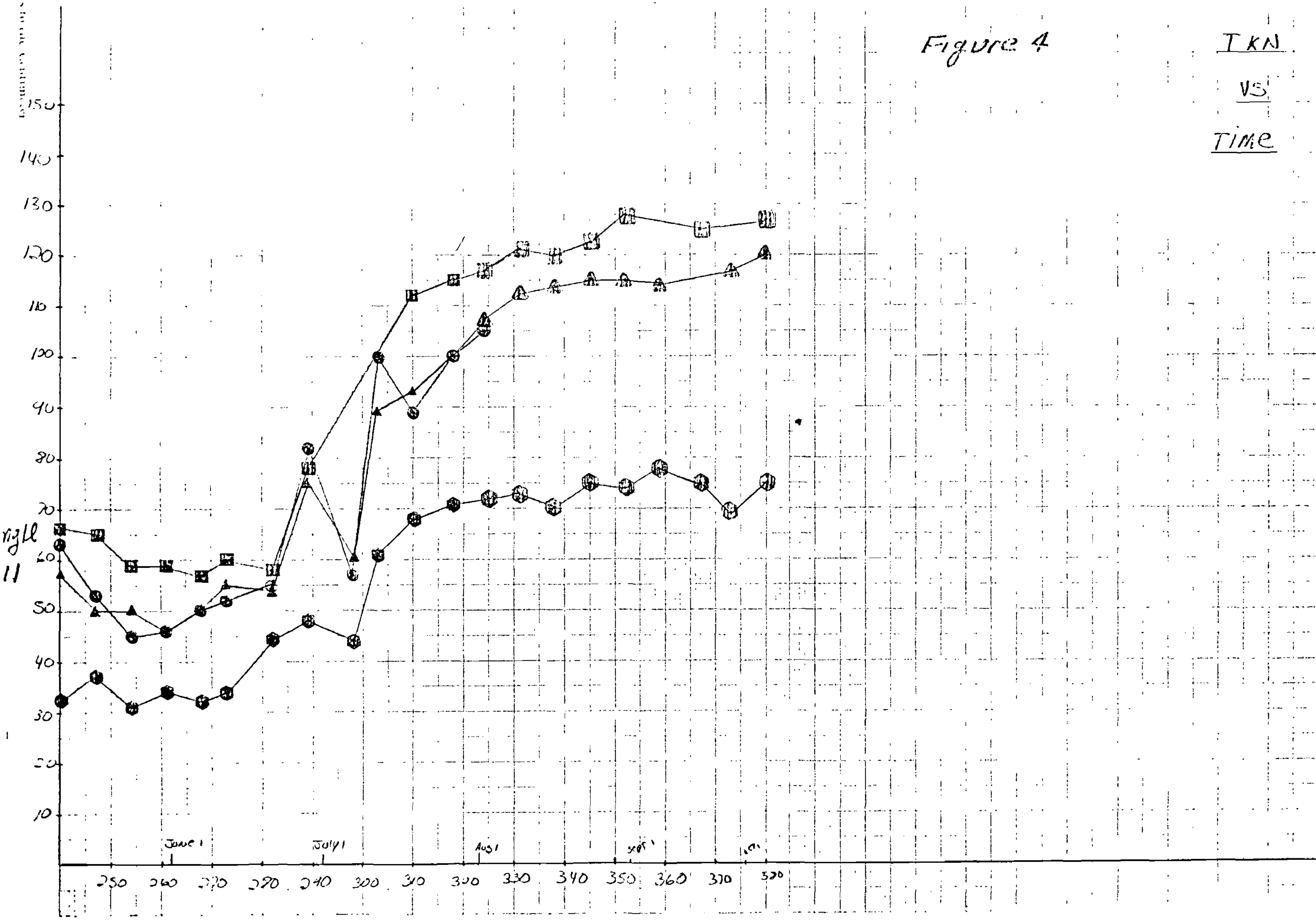


Figure 4
TKN
VS
TIME
mg/l
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
June 1
July 1
Aug 1
Sept 1
250
260
270
280
290
300
310
320
330
340
350
360
370
380

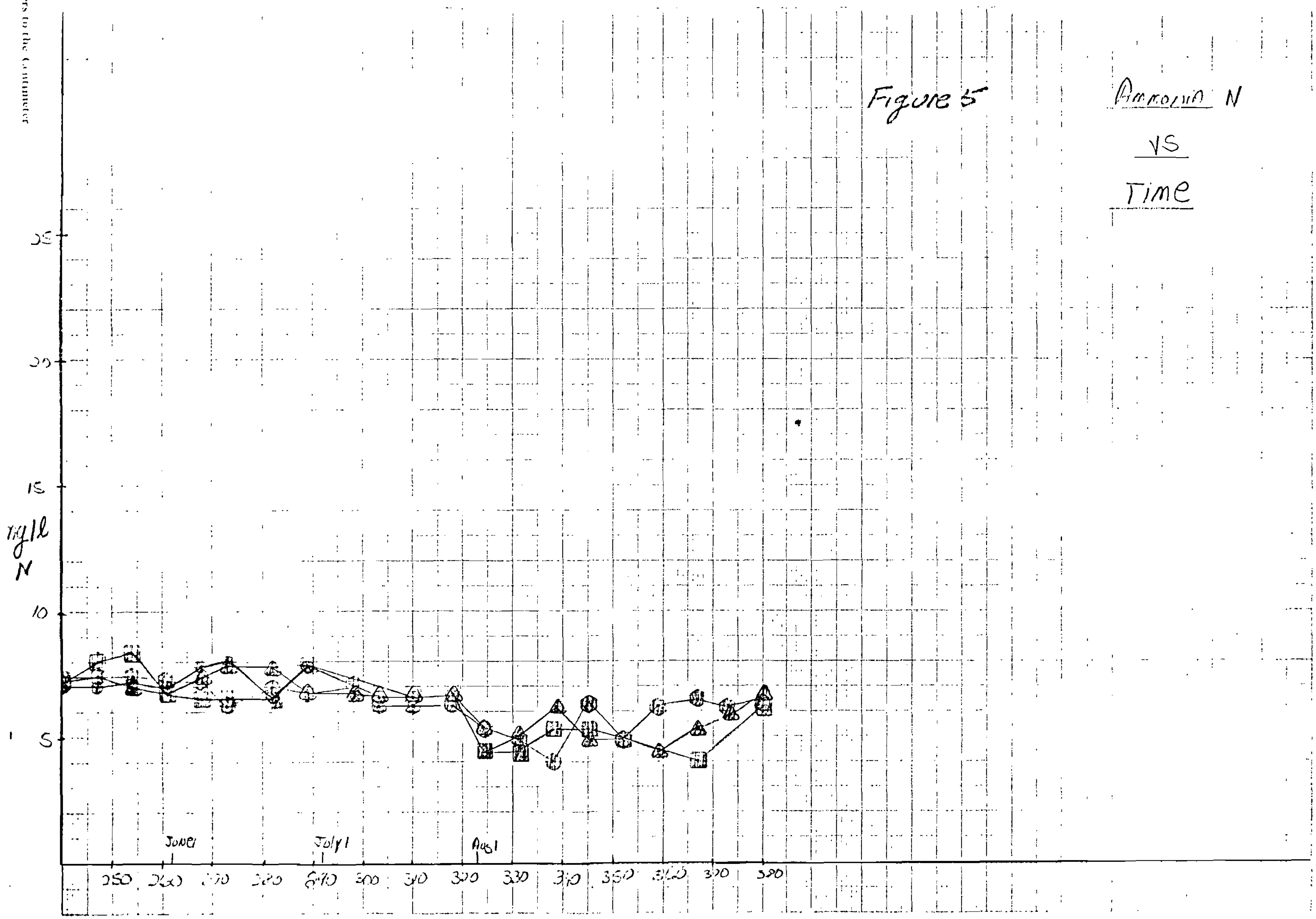
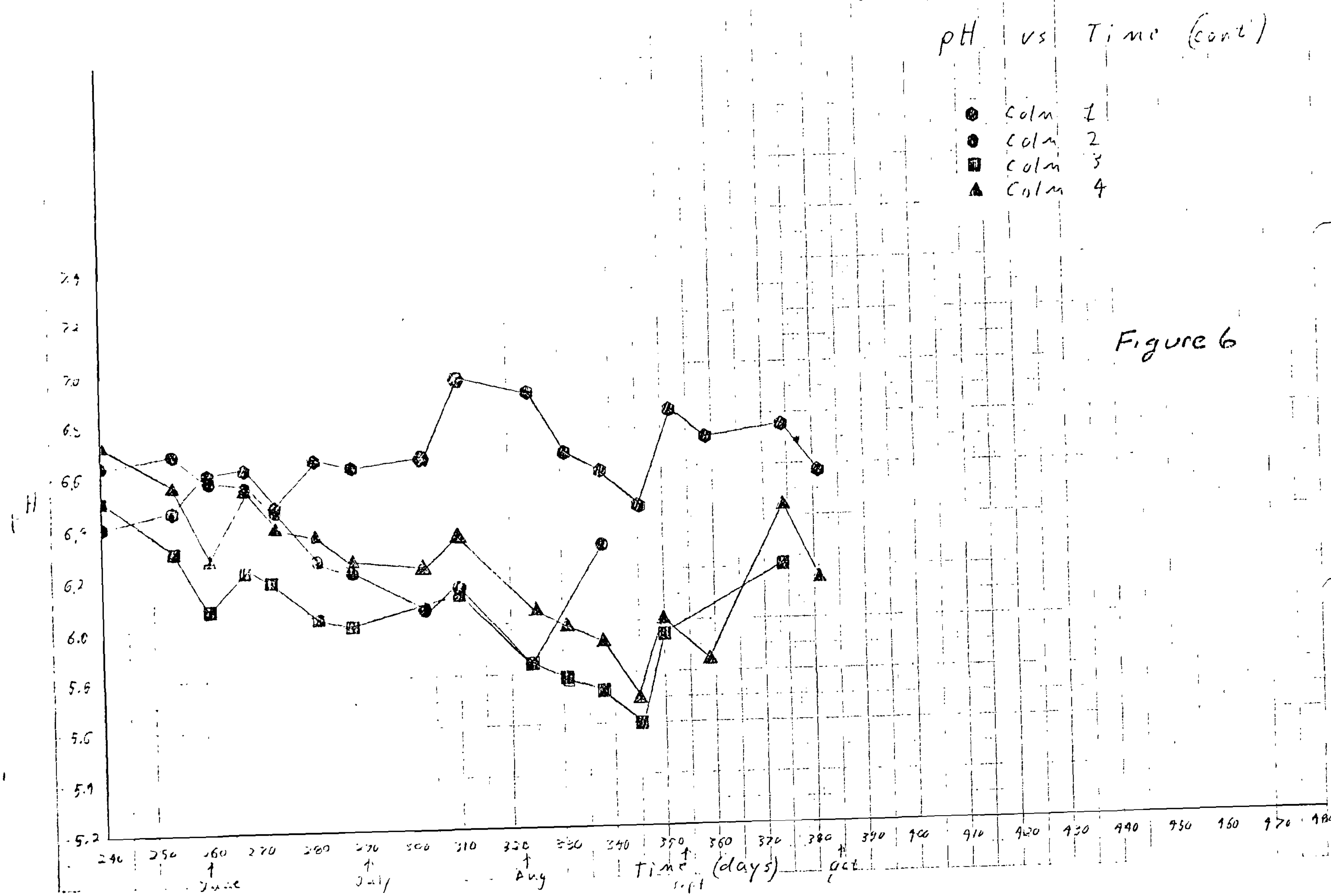
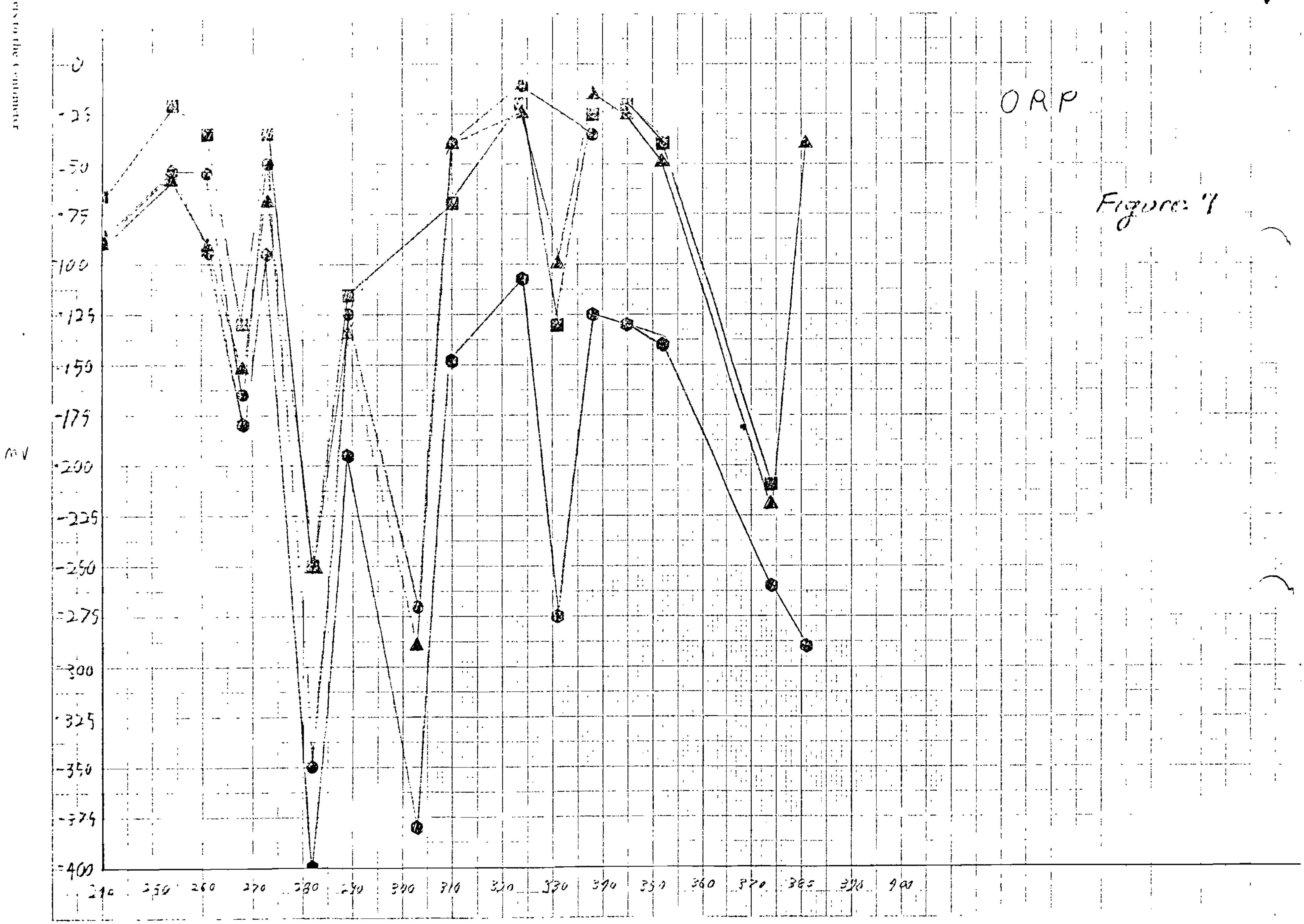


Figure 5
Ammonia N
vs
Time
mg/l
N
15
10
5
June 1
July 1
Aug 1
250
300
310
330
350


pH vs Time (cont')
Colm 1
Colm 2
Colm 3
Colm 4
pH
Time (days)
June
July
Aug
Sept
Oct
Figure 6


ORP
Figure 7
mV
0
-25
-50
-75
-100
-125
-150
-175
-200
-225
-250
-275
-300
-325
-350
-375
-400
10 Millimeters to the Centimeter

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CIVIL ENGINEERING

TELEPHONE:
(404) 894-2265

January 10, 1981

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" (E-20-666)

Dear Dirk:

Enclosed herewith is the seventh quarterly progress report on the subject research covering the period October 1, 1980 through December 31, 1980. You will note that we have had difficulties in sustaining sufficient leachate quantities to be able to continue regular leachate recycle together with routine sampling and analyses. Even with the artificial addition of moisture as tap water, dry weather continues to compound these problems and the onset of extremely cold temperatures has now suggested that we discontinue this strategy until more precipitation and/or warmer weather prevails. However, such an approach will likely defer the desired results from the studies and we consider it prudent to anticipate a need for an extension of the project.

To successfully achieve the project objectives and to permit a more thorough evaluation of the data under regular leaching and recycle, I would therefore propose that the present project period which terminates on March 22, 1981 be extended through the summer to August 31, 1981. Such an extension would also accommodate conditions for closure of the columns as well as the larger landfill cells as discussed recently with you as a separate task. As we have requested a separate funding for the larger cells, we would appreciate your consideration of some financial support for the extension of the present column studies also. Such support would be particularly pertinent in order to keep and maintain the project personnel on a regular and productive basis. If some funding for this purpose is available, I would be pleased to be advised accordingly.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

cc: Dr. J. E. Fitzgerald
Ms. Faith Costello

hb

Quarterly Progress Report No. 7
"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
October 1, 1980 - December 31, 1980

During this phase of the porject, leachate recycle was continued at frequencies of one liquid recycle per day except for Column 2 where leachate generation continued nonexistant as reported previously. By mid October, leachate generation also ceased for Columns 1 and 3 so that daily recycle was precluded. However, Column 4 continued to generate about 25 gallons of leachate accumulation which was recycled daily as it accumulated or at most, twice per day. This procedure also caused a decrease in total quantity of leachate generated in Column 4 so that by the beginning of November, only 5 gallons remained. Since the quantities of leachate available for recycle were so small and considered unrepresentative of the behavior within the columns, routine sampling and analysis was interrupted until early December 1980.

The reductions in leachate quantity were attributed to the extremely dry weather during this report period. Consequently, since no appreciable rainfall was received by the cells sufficient to allow for leachate generation, 20 gallons of tap water were added to each simulated landfill column on December 5, 1980. Immediately thereafter, some leachate was generated in each of the cells so that sampling and analysis could again be commenced. However, as recycle progressed and the dry weather continued, leachate volumes decreased to essentially nil in Column 2 and to 10, 10 and 20 gallons in Columns 1, 3 and 4, respectively. Recently, these latter volumes have also decreased so that sampling and analyses have become hampered and intermittant.

Unfortunately, the lack of precipitation in the area has been accompanied by extremely cold weather which is believed to have decelerated the processes of reaction and/or stabilization within the landfill columns. Confronted with this collective impact on the normal processes of change within the waste mass and leachate, it was decided to forego the introduction of additional tap water and to await the onset of more precipitation and warmer weather. Although this strategy may curtail the continuation of a regular leachate collection and analysis schedule, it is not considered to adversely influence the ultimate results obtained from the experimental studies, particularly if the project period can be extended.

What samples and analyses have been obtained during this report period indicate a continuation of some of the trends indicated previously. A more comprehensive tabulation of these results including updated illustrations will be included with the report of the next progress period. However, using the figures previously submitted (Progress Report No. 6), concentrations of COD (as well as BOD and TOC) appear to be decreasing and the nutrients (N,P) appear to be increasing. The former may have been due to a combination of continued removal of organic constituents coupled with a decrease in leachate volume; the latter is probably more related to a decrease in total leachate volume. The leachate pH has remained relatively constant and in the bicarbonate buffering range, ORP continues to fluctuate and the metals remain at nearly undetectable levels. Therefore, the experimental results during this phase of the project continued to reflect the capacity of the landfill environment to capture and retain heavy metal constituents when operated to contain leachate with leachate recycle.

A portion of this research work will be used to substantiate concepts of heavy metal transformation and retention in landfills at the Seventh Annual Hazardous Waste Research Symposium in Philadelphia in March 1981 for which a paper titled "Containment of Heavy Metals in Landfills with Leachate Recycle" has been preposed and submitted.

Frederick G. Pohland
Project Director

hb

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
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TELEPHONE:
(404) 894-2265

April 14, 1981

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" (E-20-666)

Dear Dirk:

Enclosed herewith is the eighth quarterly progress report on the subject research covering the period January 1, 1981 through March 31, 1981. The onset of more rainfall and warmer weather has again permitted initiation of a more routine recycle and analysis schedule. The early data indicate a reversal of the trend toward higher pollutant concentrations in the leachate of the test columns which is believed consequenced by more favorable environmental conditions and dilution effects. As more data are developed under this operational mode, attempts will be made to determine changes in masses of leachate constituent throughout the total project period. Such an analysis will better define actual behavior and ultimate fates of the heavy metals as well as other indicator parameters.

We are beginning to plan for the effort embraced by the new support and extension of the current project period through September 22, 1981. We look forward to receipt of official notification of this action.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP/hb

enclosure

cc: Dr. J. E. Fitzgerald
Ms. Faith Costello

Quarterly Progress Report No. 8
"Fate of Heavy Metals During Landfill
Stabilization of Solid Waste Materials
with Leachate Recycle
EPA Grant No. R-806498-01
Research Project E-20-666
Georgia Institute of Technology
Atlanta, Georgia
January 1, 1981 - March 31, 1981

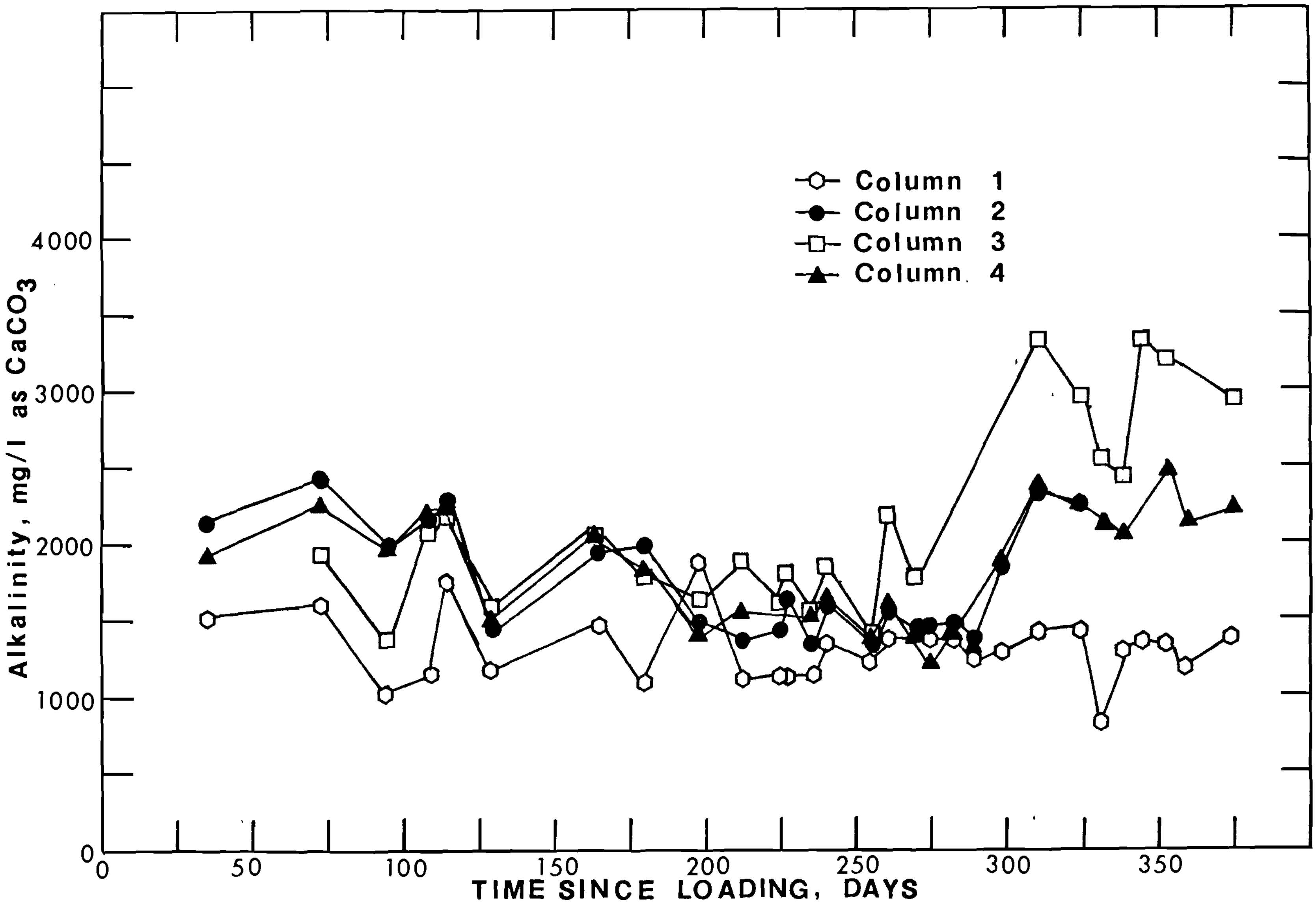
During this phase of the project, precipitation has increased in the project area, thereby allowing for the accumulation of sufficient leachate to again initiate a routine recycle schedule of once per day. This renewed exposure of the leachate to the test column contents, coupled with the onset of warmer temperatures, should provide an appropriate setting for continued and unimpeded activity within the columns. The impact of this procedure is beginning to be observed in the behavior of the test parameters, but data are yet inconclusive. Trends do indicate, however, that the gradual rise in some of the leachate constituents observed during the previous report period is beginning to taper off and a decrease to low contaminant levels has commenced. This change is believed to have been consequenced by both the more favorable environmental conditions as well as the increase in leachate volume and hence dilution of constituents.

The overall effect of dilution throughout the project phases is presently being carefully scrutinized in order to develop experimental evidence of changes in leachate constituents on a mass basis. Both leachate volumes and calculations with inherent conservative tracers (chlorides) will be used in this evaluation together with observations on temperature and other climatic considerations. This analysis is deemed necessary to properly assess the reactivity and/or mobility of leachate constituents and in particular, the fate of the heavy metals originating from the industrial plating sludge. Results of this effort will be reported in detail at the end of the next project period.

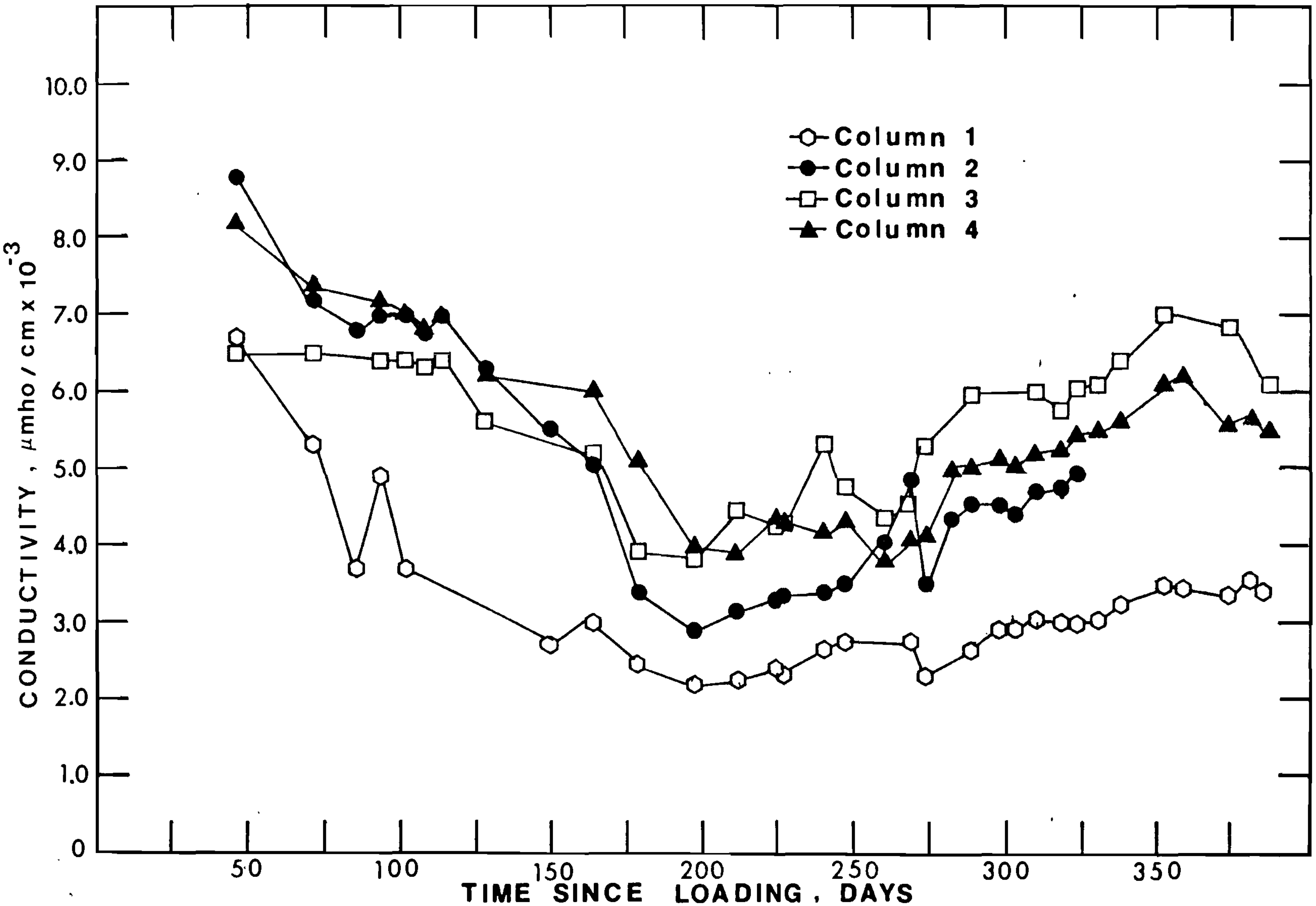
In anticipation of new funding support and an extension of the project through September 22, 1981, preparations are being made to provide for the analysis of biochemically stabilized leachate samples for the possible presence of priority pollutants and refractory substances. In addition, the contents of each column and its appurtenances will be disassembled and inspected for both visual and analytical changes. The final location and/or degree of alteration of the refuse and sludge constituents within the columns will be of particular interest as will evidence as to the nature of conditions prompting removal of the heavy metals. This effort will be culminated toward the end of the extended project period.

During the current project period, some of the research results were presented formally at the Seventh Annual Research Symposium, Land Disposal of Municipal Solid and Hazardous Waste and Resource Recovery, March 16-18, 1981 in Philadelphia. The title of the presentation was "Containment of Heavy Metals in Landfills with Leachate Recycle" and dealt with the possible reactions that would lead to the mobilization or immobilization of heavy metals in a landfill environment. In addition to the data included in the text of this presentation, the attached figures provide companion information on alkalinity, COD, zinc and cumulative moisture addition through the period covered. To resolve any confusion caused by the mislabeling of the figure in the presentation, the figure on conductivity is also attached.

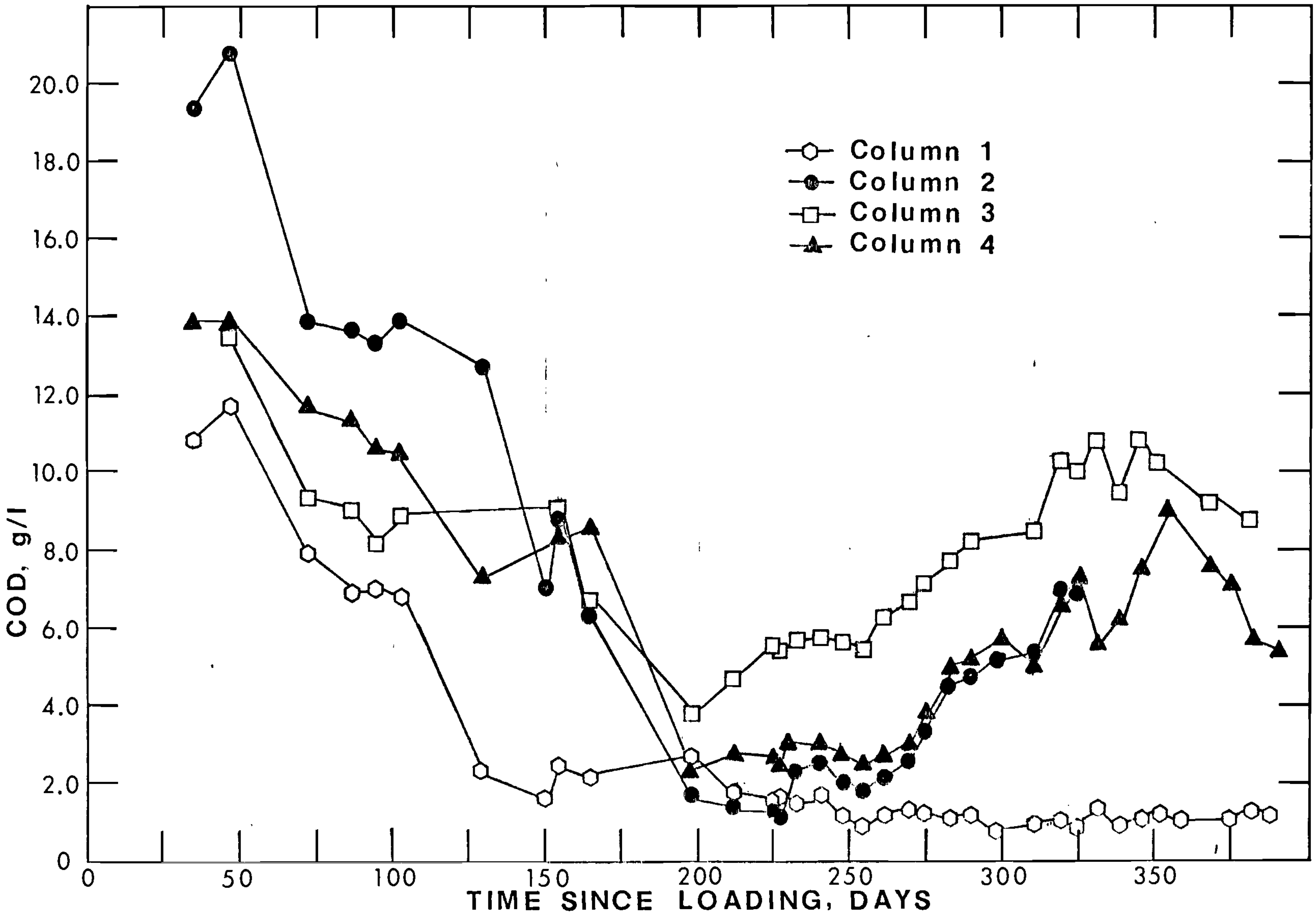
Frederick G. Pohland
Project Director

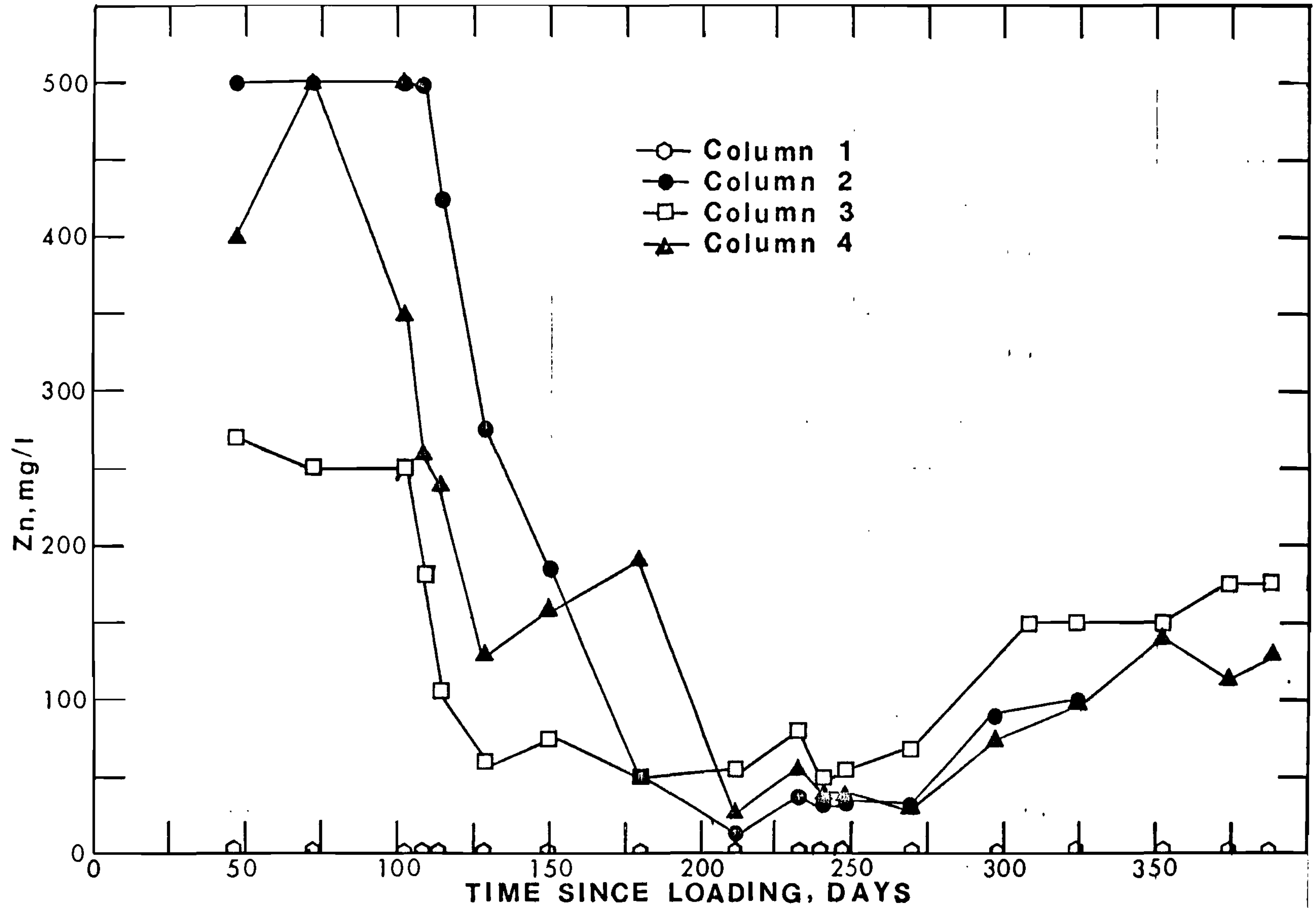


Column 1
Column 2
Column 3
Column 4
Alkalinity, mg/l as $CaCO_3$
0
1000
2000
3000
4000
0
50
100
150
200
250
300
350
TIME SINCE LOADING, DAYS

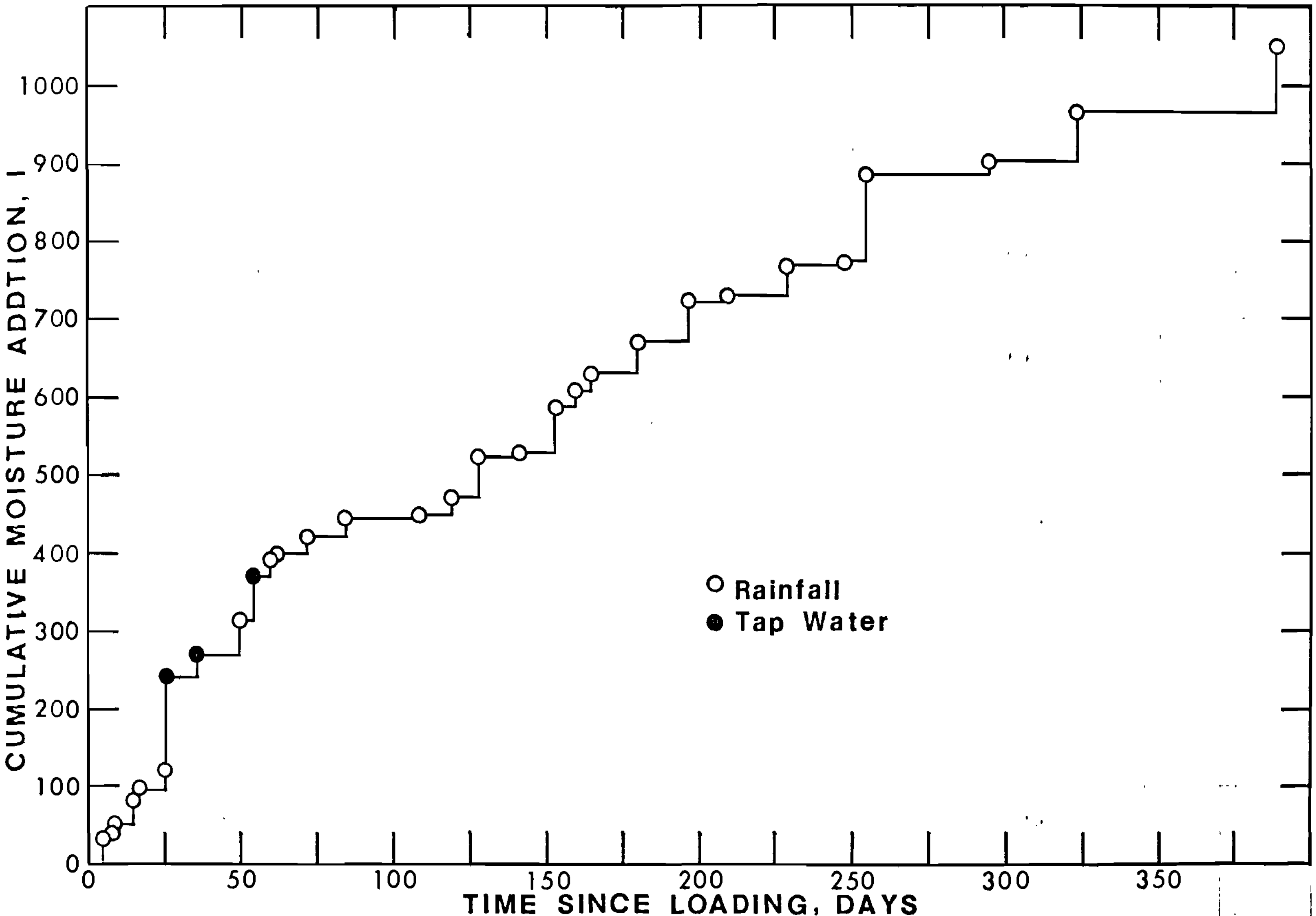


Column 1
Column 2
Column 3
Column 4
CONDUCTIVITY, μmho / cm x 10^-3
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
50
100
150
200
250
300
350
TIME SINCE LOADING, DAYS


Column 1
Column 2
Column 3
Column 4
COD, g/l
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
0
50
100
150
200
250
300
350
TIME SINCE LOADING, DAYS



Column 1
Column 2
Column 3
Column 4
Zn, mg/l
0
100
200
300
400
500
0
50
100
150
200
250
300
350
TIME SINCE LOADING, DAYS


CUMULATIVE MOISTURE ADDTION, l
TIME SINCE LOADING, DAYS
Rainfall
Tap Water
0
100
200
300
400
500
600
700
800
900
1000
0
50
100
150
200
250
300
350

GEORGIA INSTITUTE OF TECHNOLOGY
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July 14, 1981

Mr. Dirk Brunner, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" (E-20-666)

Dear Dirk:

Enclosed herewith is the ninth quarterly progress report on the subject research covering the period April 1, 1981 through June 30, 1981. The results provided were discussed during your recent visit and reflect the general stabilization patterns reported previously except for the increases in pollutant strengths for test columns Nos. 3 and 4. It is too early to definitely determine the causes of these changes, but we suspect it was a combination of warmer weather and a removal of stresses to an extent that permitted more active biological populations, at least of the acid formers. Most recent data (not reported herein) suggest a reversal of this trend which may then lead to a similar extent of stabilization as observed in columns Nos. 1 and 2.

We appreciate your continued support and interest in our research efforts. Further interpretations of landfill behavior in the test columns will be included in our next report.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP/hb

enclosure

cc: Dr. J. E. Fitzgerald
Ms. Faith Costello

E 20 (/G.E.
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Quarterly Progress Report No. 9

"Fate of Heavy Metals During Landfill
Stabilization of Solid Waste Materials
with Leachate Recycle"

EPA Grant No. R-806498
Research Project E-20-666 /G.E.

Georgia Institute of Technology
Atlanta, Georgia

April 1, 1981 - June 30, 1981

During this phase of the project, operation of the simulated landfill columns continued with leachate recycle on a daily basis. This, together with the onset of warm weather and perhaps a decrease in combined stress of the industrial waste constituents, has led to a resumption of volatile acid production in test columns Nos. 3 and 4. This production has been confirmed by volatile acids determinations and is reflected in the attached figures for COD and BOD_5. Compared to the leachate from Column 1 and 2, this increase is rather striking, leading to the possibility that inhibition in the columns with the highest metals content has been overcome and normal processes of biological conversion are proceeding more effectively. Most recent data, not illustrated herein, suggest conversion of the volatile acids to gas with corresponding decreased in leachate COD and BOD_5.

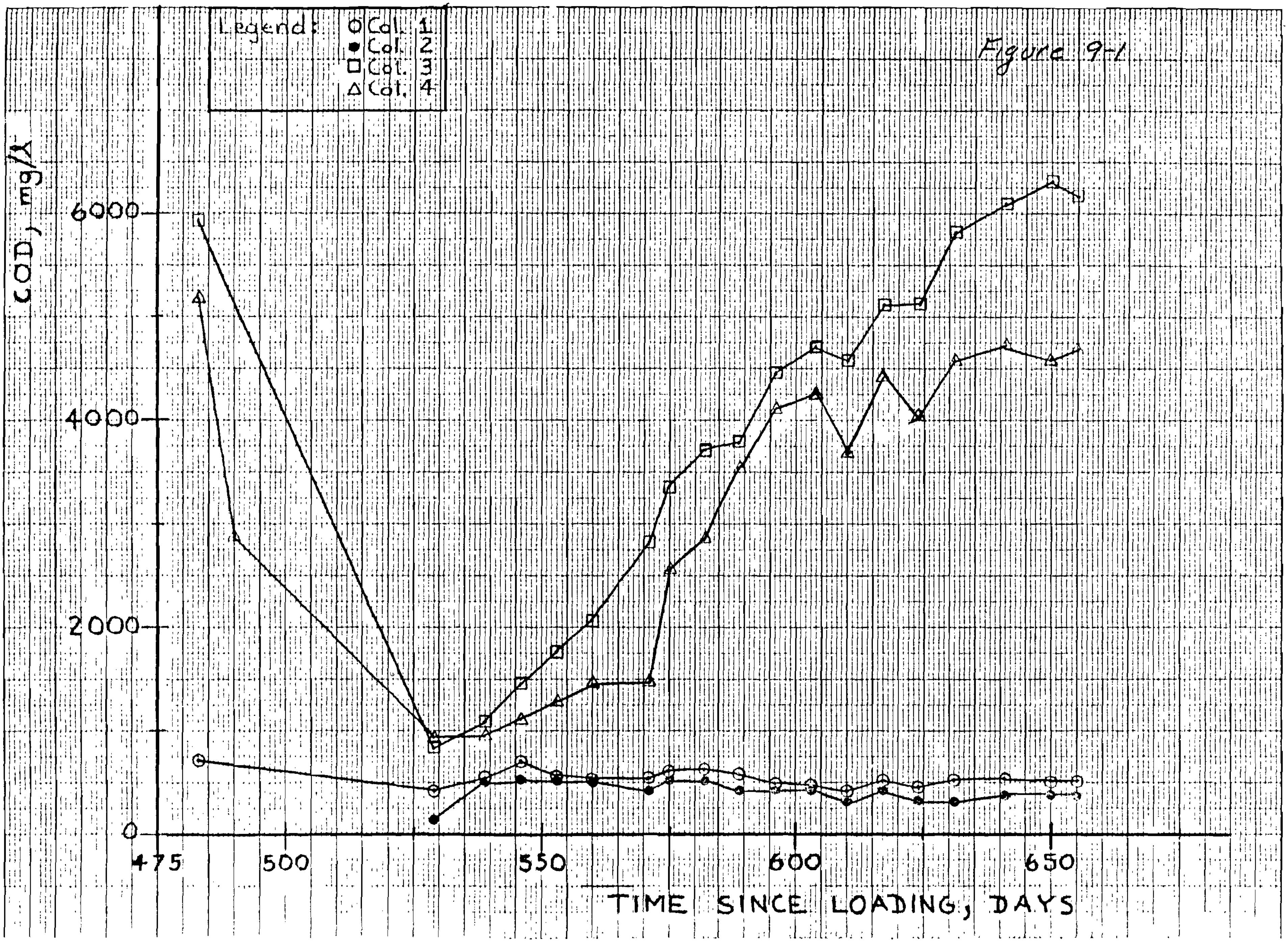
In general, the leachate pH has changed with the production of volatile acids particularly in Columns 3 and 4 where decreases in leachate pH occurred commensurate with the production of volatile acids and increasing alkalinity. (See pertinent figures attached). The abrupt increase in leachate pH in Column 2 from neutral for a short period was not anticipated and has not yet been explained. Column 2 leachate, however, tends to have the lowest buffer capacity (alkalinity) which would make it more vulnerable should any amounts of base be released from the refuse mass. The leachate in Column 2 also has changed more erratically than that in the other columns which may help to explain this behavior.

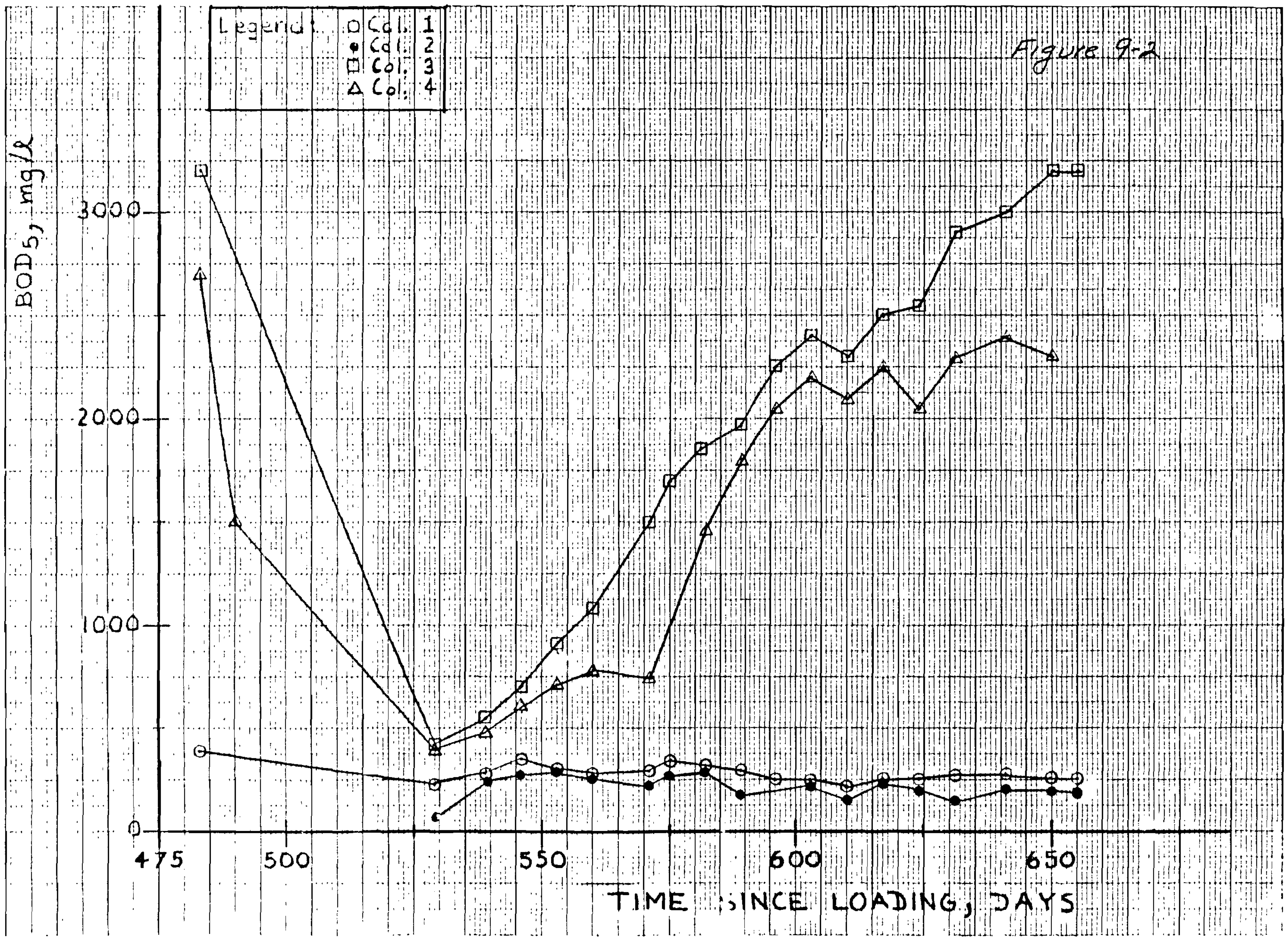
Regarding the heavy metals, the attached figures indicate the dependency of relative metal mobility on pH. As the pH (and volatile acids) changed to promote more acid conditions, the metals appeared to become more concentrated in the leachate particularly for Columns 3 and 4. These trends would be expected; reductions in volatile acids and increases in pH should again decrease soluble metal concentrations. Since the increases in volatile acids and metals in the leachates contribute to the conductivity, similar increases in conductivity would be expected to and did occur. The absolute solubility of the metals would be affected by conductivity because of the activity implications on equilibrium considerations. This concept will be further developed in the final analysis of all the experimental data.

The measurable presence of sulfides has undoubtedly contributed to a supression of heavy metal toxicity in the test columns with the results indicating that the effect has been eliminated in the leachates from Columns 1 and 2. Since sulfides continue to persist and ORP values are favorable for reduction and precipitation reactions to occur, continued removals of metals would be anticipated particularly as the leachate in Columns 3 and 4 continues to stabilize. These interrelationships will also be discussed in more detail at the end of the study period.

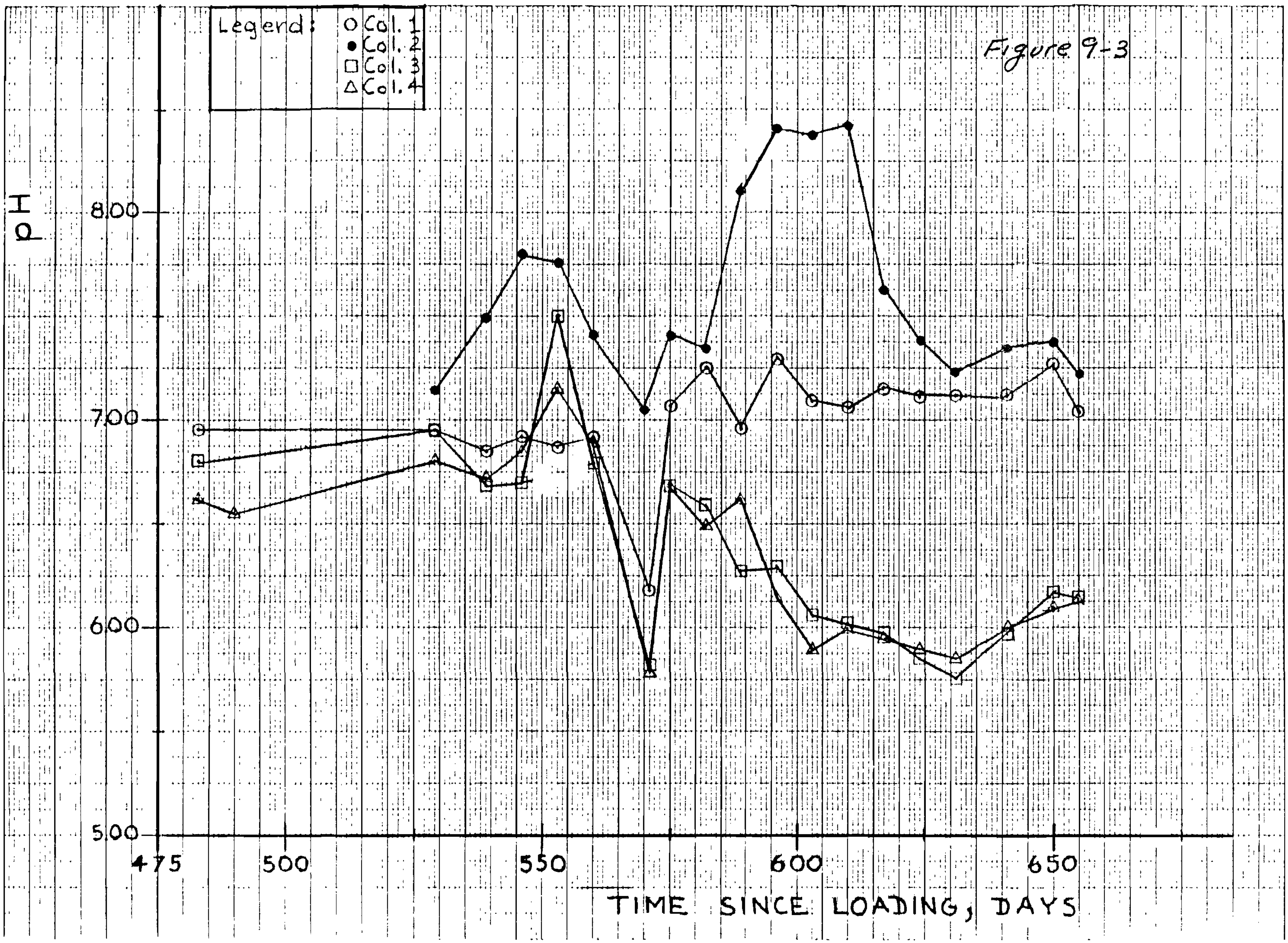
Increased rainfall has served to enhance renewed stabilization and availability of leachate for recycle. Here, conservative - type tracers (chlorides, sodium, potassium) will be evaluated to determine possible dilution effects on concentration data. In addition, once active biological stabilization ceases in all of the columns, the columns will be opened and examined for their remaining characteristics for comparison with the efforts now being conducted on the previous test cells. It is anticipated that all of these efforts will be concluded at the end of the next project period.

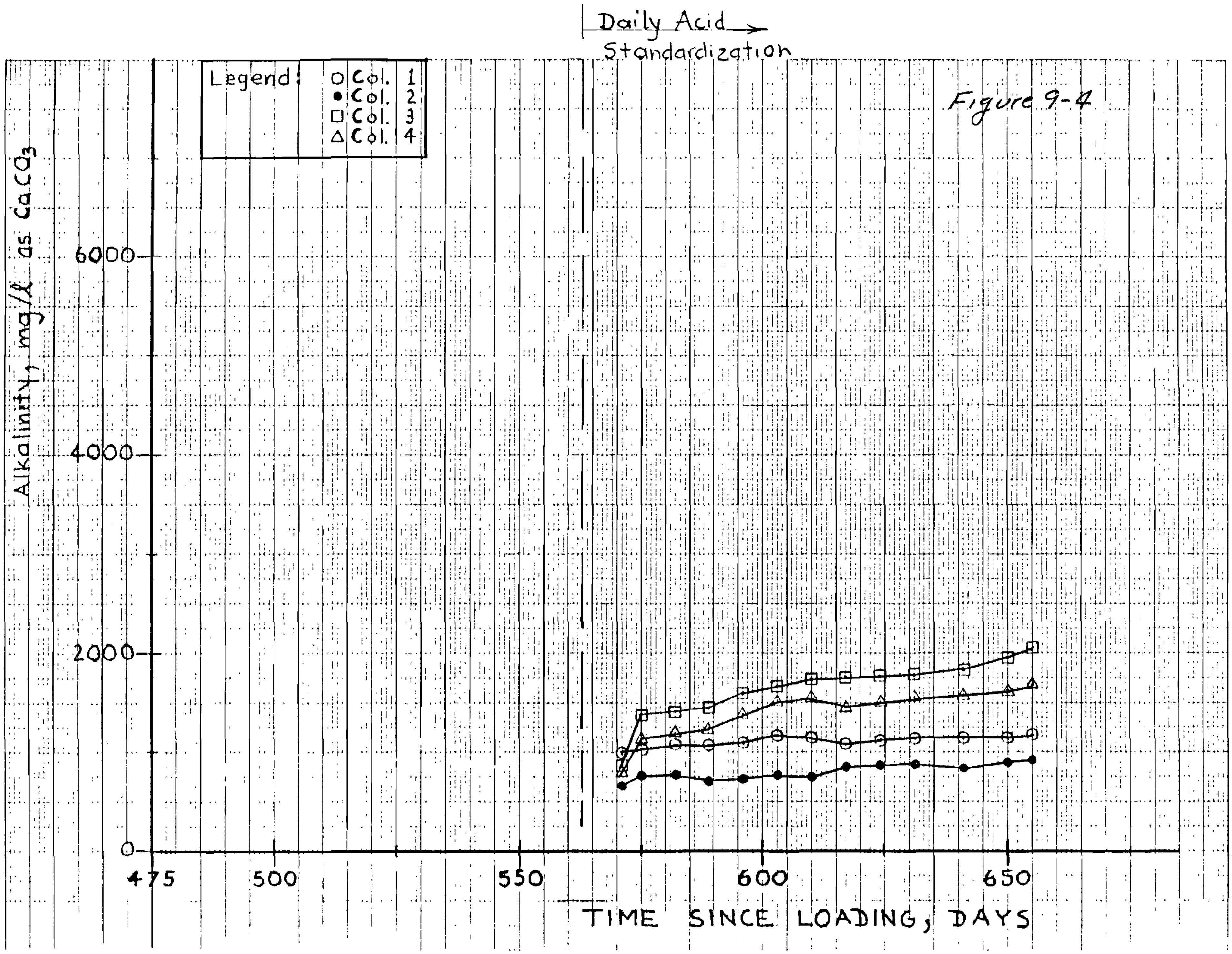
Frederick G. Pohland
Project Director


Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-1
COD, mg/l
6000
4000
2000
0
475
500
550
600
650
TIME SINCE LOADING, DAYS

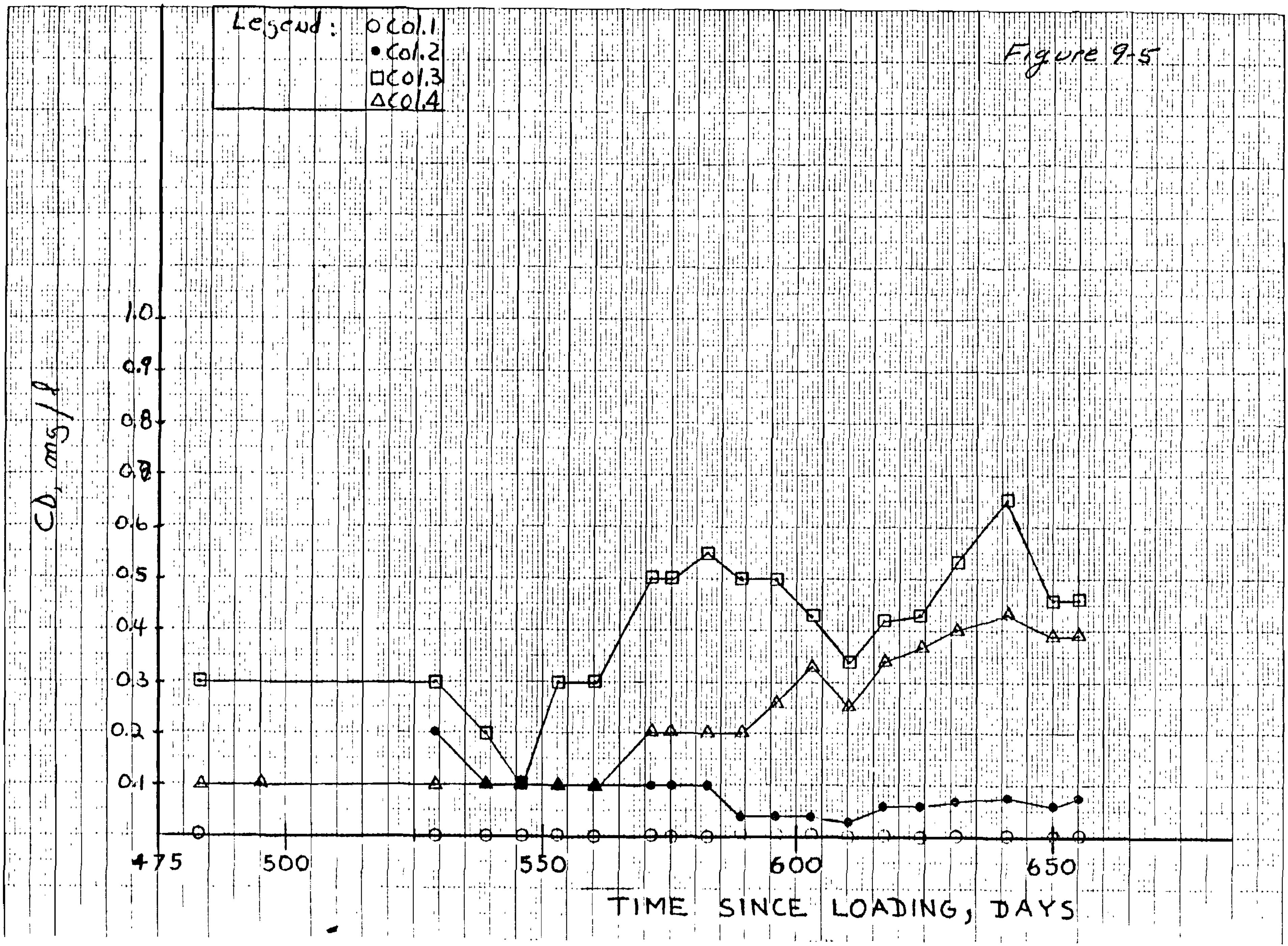


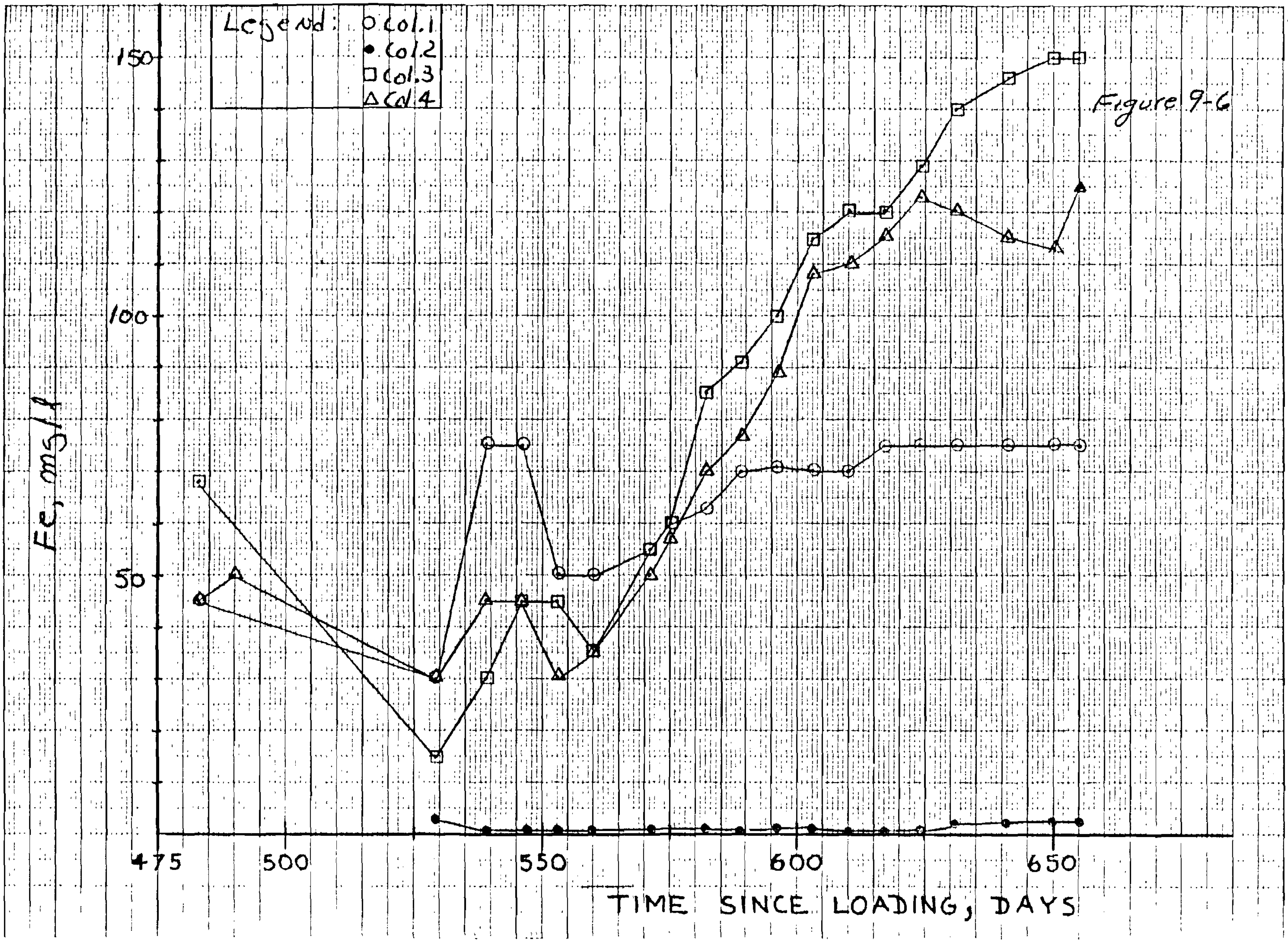
Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-2
BOD5, mg/l
3000
2000
1000
0
475
500
550
600
650
TIME SINCE LOADING, DAYS

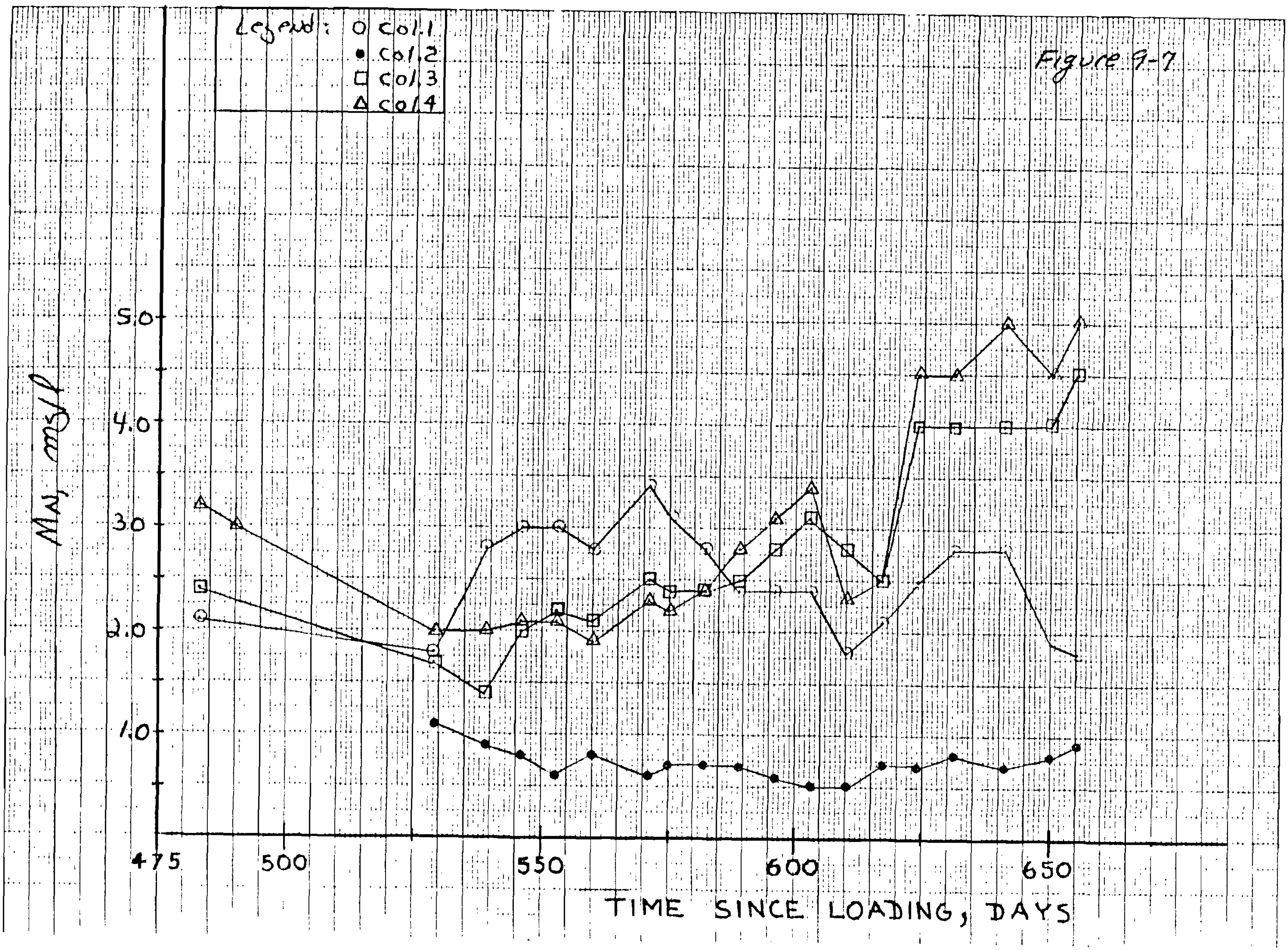

Legend:
○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-3
pH
8.00
7.00
6.00
5.00
475
500
550
600
650
TIME SINCE LOADING, DAYS



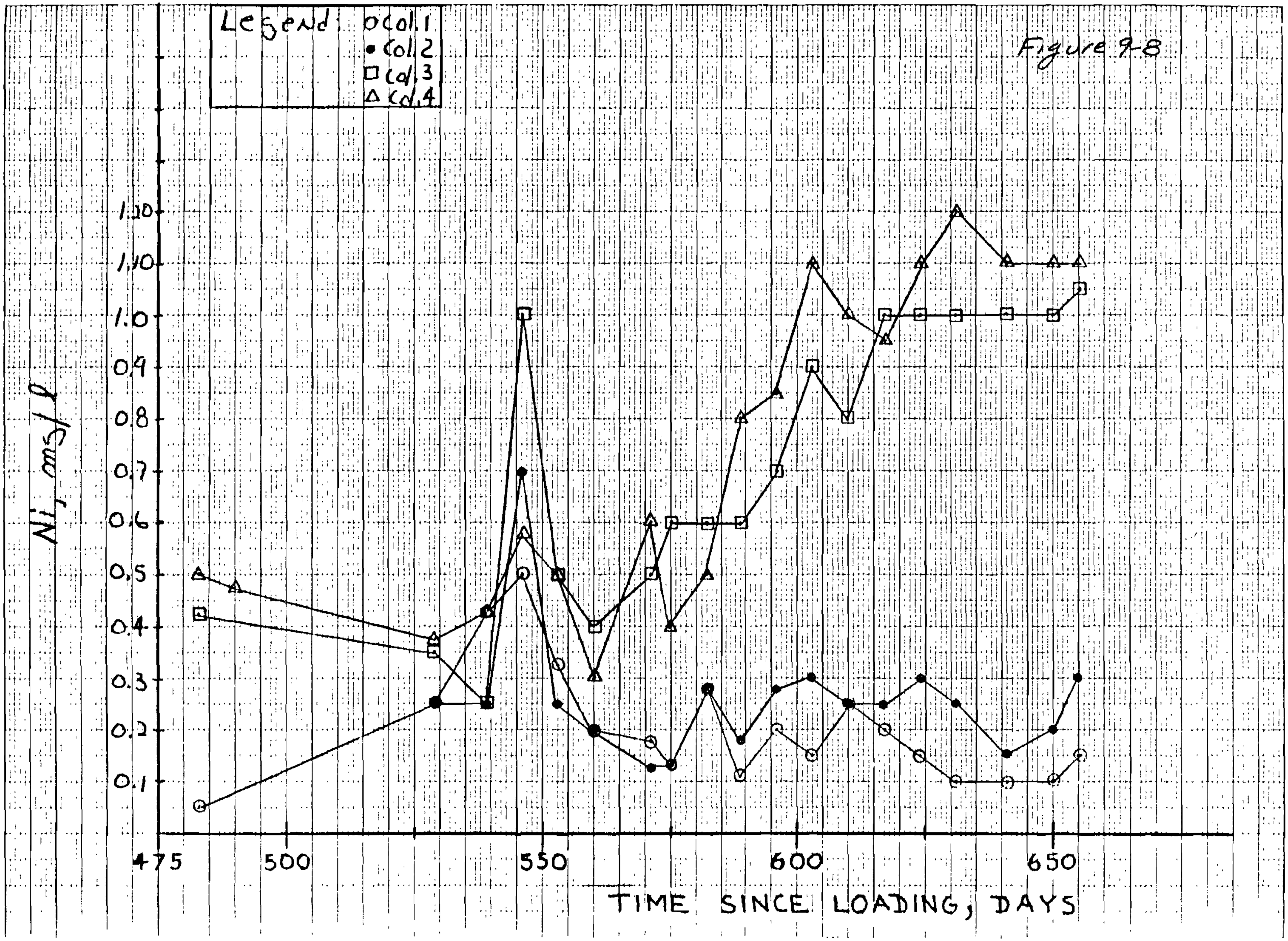
Daily Acid Standardization
Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-4
Alkalinity, mg/ℓ as CaCO3
6000
4000
2000
0
475
500
550
600
650
TIME SINCE LOADING, DAYS


Legend:
○ Col.1
● Col.2
□ Col.3
△ Col.4
Figure 9-5
CD, mg/l
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
475
500
550
600
650
TIME SINCE LOADING, DAYS

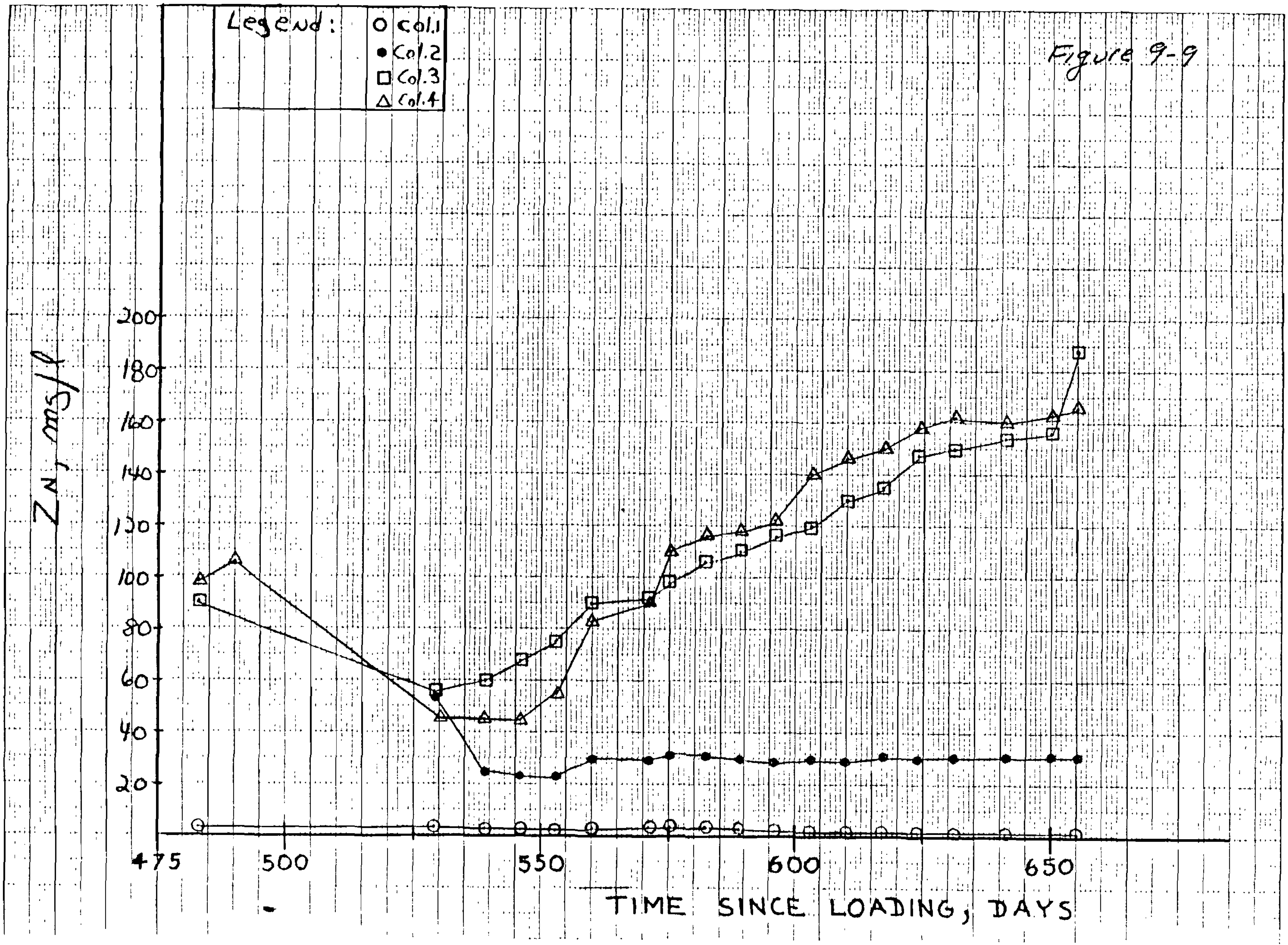

Legend:
○ Col.1
● Col.2
□ Col.3
△ Col.4
Figure 9-6
Fe, mg/l
150
100
50
475
500
550
600
650
TIME SINCE LOADING, DAYS

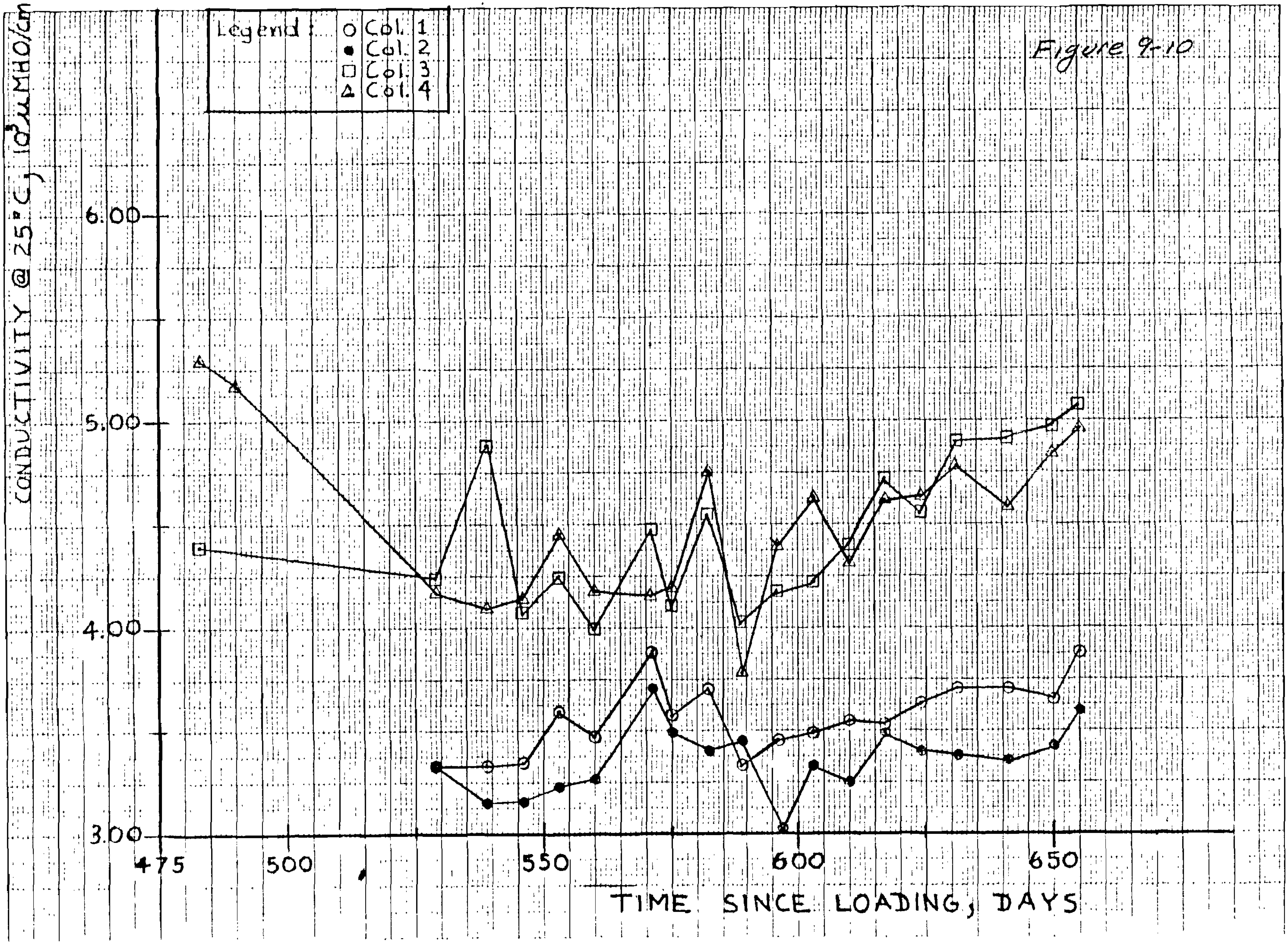


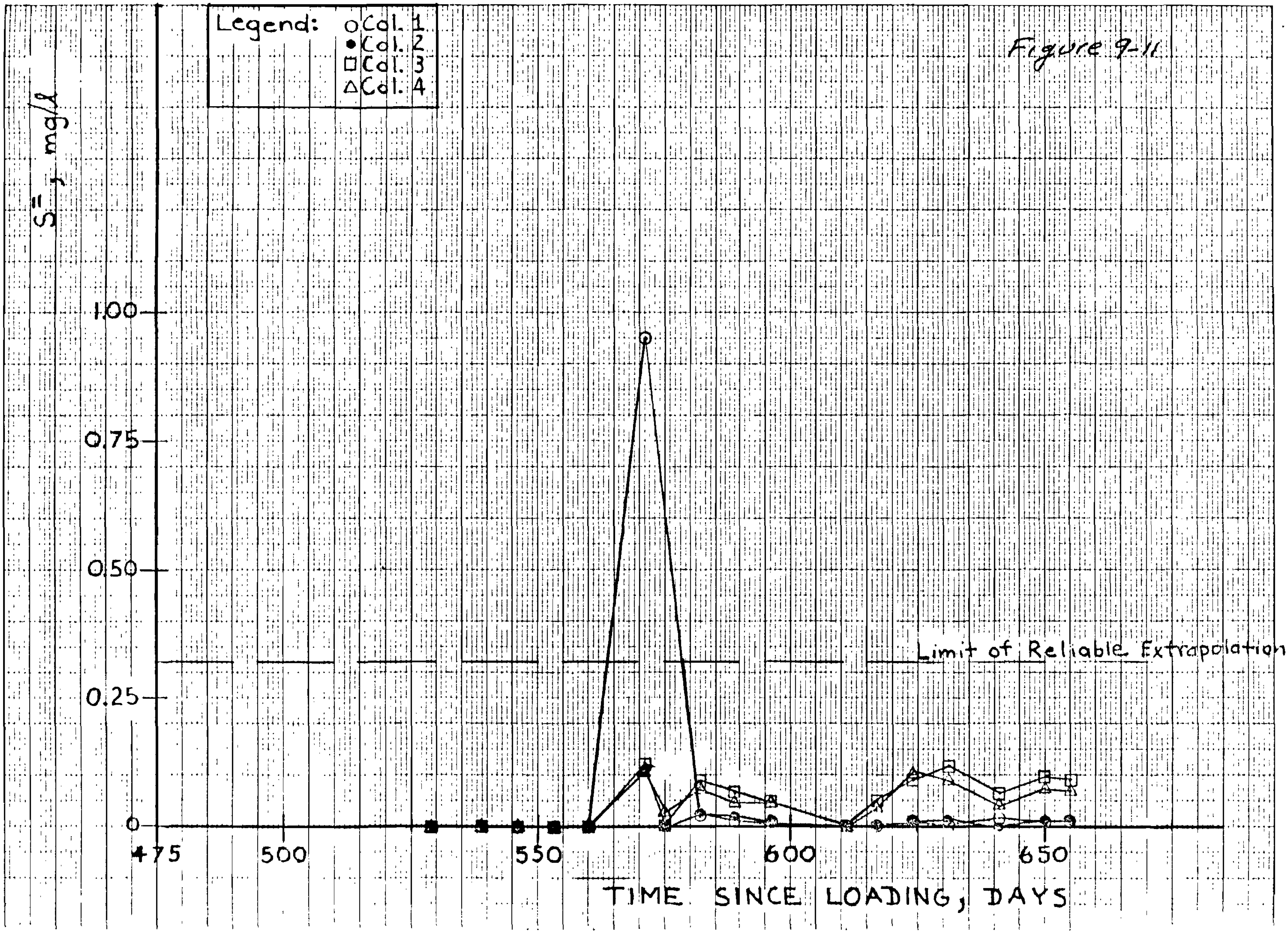
Legend: ○ Col.1
● Col.2
□ Col.3
△ Col.4
Figure 9-7
Mv, m²/kN
5.0
4.0
3.0
2.0
1.0
475
500
550
600
650
TIME SINCE LOADING, DAYS



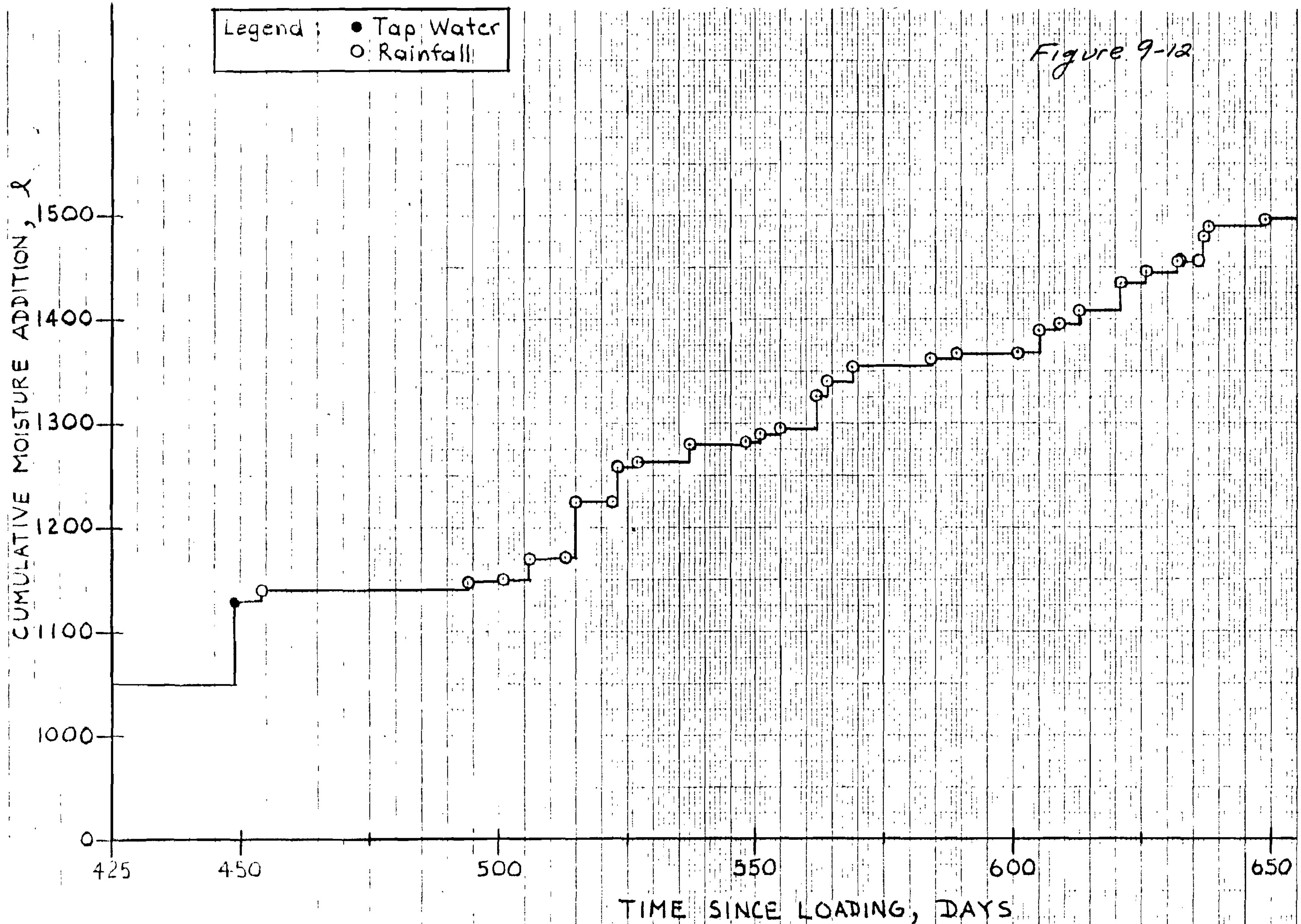
Legend: o Col. 1
• Col 2
□ Col 3
△ Col 4
Figure 9-8
Ni, mg/l
1.20
1.10
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
475
500
550
600
650
TIME SINCE LOADING, DAYS

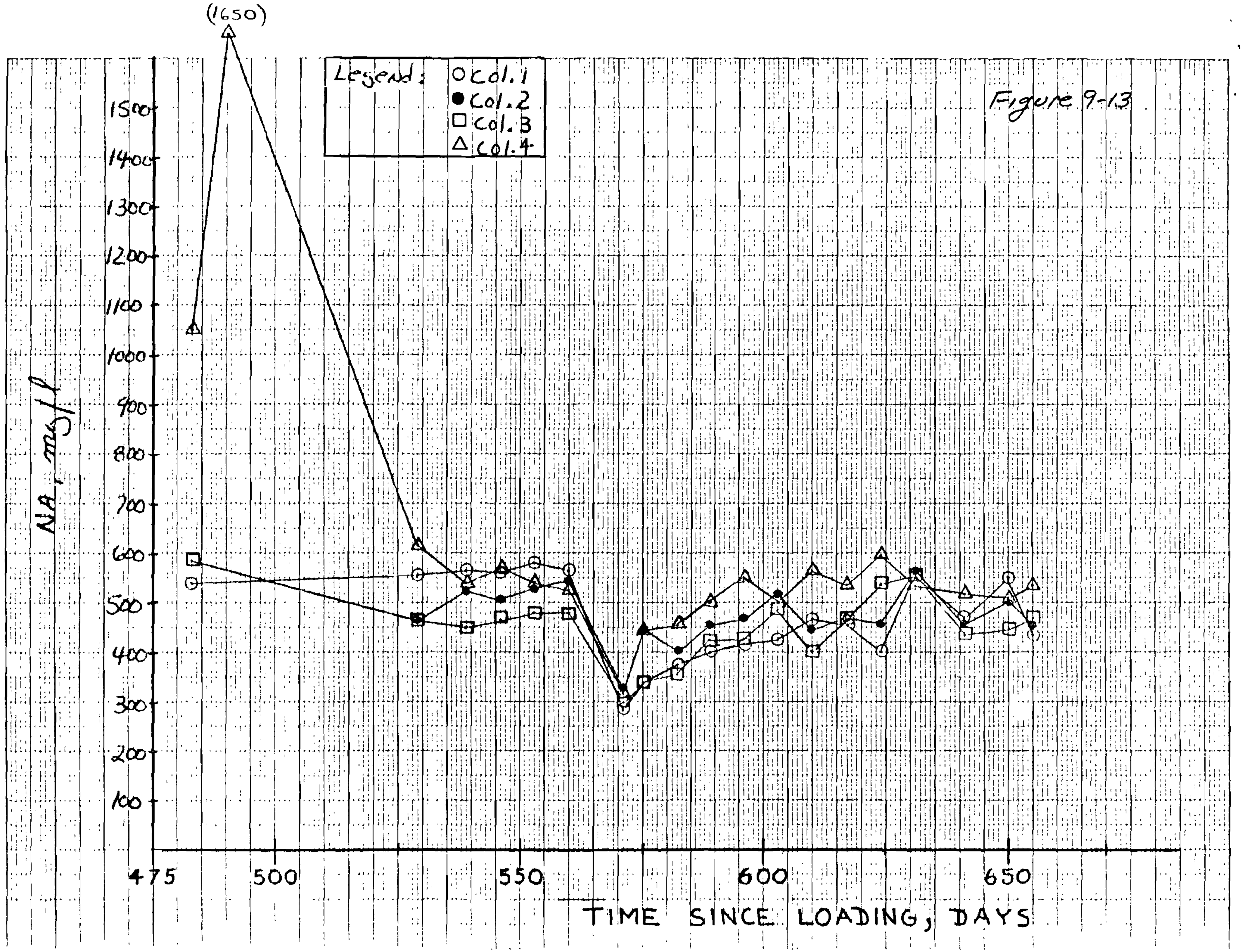

Legend:
○ Col.1
● Col.2
□ Col.3
△ Col.4
Figure 9-9
ZN, mg/l
200
180
160
140
120
100
80
60
40
20
475
500
550
600
650
TIME SINCE LOADING, DAYS

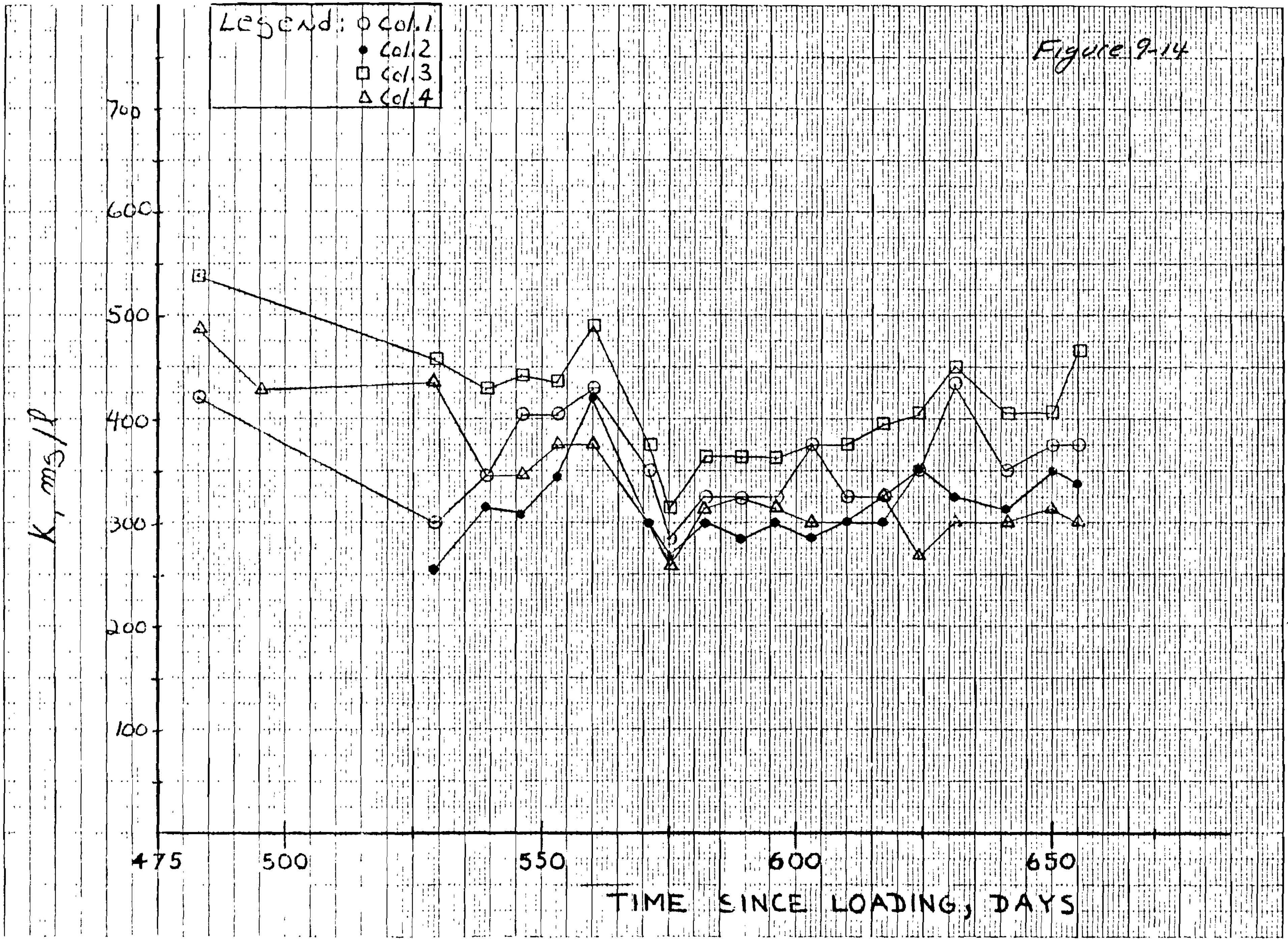

Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-10
CONDUCTIVITY @ 25°C, 10³ μMHO/cm
6.00
5.00
4.00
3.00
475
500
550
600
650
TIME SINCE LOADING, DAYS



Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-11
$S^=$, mg/l
1.00
0.75
0.50
0.25
0
475
500
550
600
650
Limit of Reliable Extrapolation
TIME SINCE LOADING, DAYS


Legend: ● Tap Water
○ Rainfall
Figure 9-12
CUMULATIVE MOISTURE ADDITION, ℓ
0
1000
1100
1200
1300
1400
1500
425
450
500
550
600
650
TIME SINCE LOADING, DAYS


(1650)
Legend:
Col. 1
Col. 2
Col. 3
Col. 4
Figure 9-13
NA, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
475
500
550
600
650
TIME SINCE LOADING, DAYS


Legend: ○ Col. 1
● Col. 2
□ Col. 3
△ Col. 4
Figure 9-14
700
600
500
400
300
200
100
K, ms/ρ
475
500
550
600
650
TIME SINCE LOADING, DAYS

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
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(404) 894-2265

October 12, 1981

Mr. Mike Roulier, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" (E-20-666)

Dear Mike:

Although I have not been formally advised, it is my understanding that you have been assigned the project manager responsibility previously held by Dirk Brunner for the subject research effort. Therefore, I have enclosed herewith our tenth quarterly progress report covering the period July 1, 1981 through September 30, 1981. This report is a follow-up to our last summary sent to Dirk Brunner on July 14, 1981.

We are presently engaged in attempting to make current our data analyses and yet continue routine operation of the landfill columns under the constraints of limited budget resources. As indicated in my October 1, 1981 correspondence and discussion with you, this budget situation is critical and unless we can obtain the relief indicated, we will be forced to terminate the experiments which have already been extended beyond what was originally planned and supported.

In order for the research effort to be continued, it is imperative that I receive a formal response to our support request. Without a positive indication of availability of commensurate support, I will not be able to maintain our research team intact.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP:pc
cc Dr. J. E. Fitzgerald, CE
Ms. Faith Costello, OCA

Quarterly Progress Report No. 10

"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"

EPA Grant No. R-806498
Research Project E-20-666

Georgia Institute of Technology
Atlanta, Georgia

July 1, 1981 - September 30, 1981

During this phase of the project, operation of the four simulated landfill columns was continued with leachate collection and recycle on a daily basis. Since this phase extended through the warm and exceedingly dry summer period, evaporative losses of moisture from all the simulated landfill columns were high and necessitated the addition of liquid (110 liters of tap water) to each column to provide enough leachate to manage and sample. As during other similar instances, the addition of water influenced the response of the columns as reflected in the pollutant characteristics in the leachates. Although this alternating dry/wet condition has caused the analytical parameters to change somewhat unpredictably, such changes are considered to actually more closely simulate landfilling conditions in the field.

Because it has been recognized that the moisture balance in each test column could greatly influence the mass of materials being released and/or attenuated, particularly in the columns where metal plating sludge was included, much of the present effort is being devoted to the adjustment of concentration data for dilution or evaporation effects. In some cases where constituent concentrations are low, such an adjustment does not appear to be significant; in others, where constituent concentrations are high or relatively reactive, the adjustment is vital to proper interpretive analysis. Consequently, all of the recorded data for significant analytical parameters are being adjusted for the entire experimental period to date. This adjustment for evaporation/dilution is being based upon the behavior of the chloride concentrations, a conservative constituent in the respective leachates, and will be reported in detail at the end of the next experimental phase.

In general, the three test columns receiving the metal plating sludges continue to exhibit a retardation of stabilization processes and, therefore, a prolongation of the presence of both inorganic and organic leachate constituents. In contrast, the control column continues to exhibit stability with the low concentrations of pollutants following trends previously reported. There does appear to be a greater microbiological activity in the test column having the lowest metal sludge content (Column 2) so that analytical results with respect to the pollutant parameters, COD, BOD_5, TOC and volatile acids indicate a resurgence of activity. This renewed activity may have been due to warmer temperature conditions coupled with the effect of moisture additions.

The other two test columns (Columns 3 and 4) continue to indicate a retarded or inhibited biological conversion with higher residual COD, BOD_5, TOC and volatile acids concentrations in the leachates and concomitantly lower pH values. This variation from the leachate character of Columns 1 and 2 will be further substantiated with the aforementioned adjustment for dilution and/or evaporation effects. It will also be analyzed to indicate a possible metal sludge loading limit below which the microbial processes of waste stabilization could proceed unimpeded.

As could be expected, the presence of the metal plating sludge in the test columns has also provided a modification of the chemical environments within the respective waste masses. This modification has been reflected not only in retarded stabilization, but in the leachate quality with respect to certain indicator parameters. Considering the nature of the metal plating sludges, with the excess availability of a basic, metal and sulfate containing mixture, the fate of the heavy metals during waste stabilization has been influenced by related chemical impacts on pH and ORP. Although both sulfides and reduced ORP conditions are present in all the column leachates, with the probability of precipitation and removal with leachate recycle of metals as sulfides, preliminary analyses suggest that the mobility of the metals may also be strongly influenced by both *in situ* hydroxide and more probably, carbonate, equilibria. This possibility is being further evaluated by examining the effects of pH and ORP on the fate of the predominant heavy metals under prevailing concentration conditions. Such an analysis will also be useful in the overall assessment of the changes in other analytical parameters.

During the next project phase, the experiments will be continued as long as viable funding continues. A manuscript entitled "The Reactivity and Fate of Heavy Metals during Landfill Disposal of Solid and Hazardous Wastes" will also be prepared for presentation at the Eighth Annual EPA Research Symposium on Solid and Hazardous Wastes scheduled for Cincinnati, Ohio March 8-10, 1982.

Frederick G. Pohland
Project Director

E-20-666

GEORGIA INSTITUTE OF TECHNOLOGY
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SCHOOL OF
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(404) 894-2265

January 29, 1982

Mr. Mike Roulier, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle" (E-20-666)

Dear Mike:

Enclosed find the eleventh quarterly progress report for the subject project covering the period October 1, 1981 through December 31, 1981. This report was delayed somewhat by some of the problems encountered in continuing the project according to the schedule originally outlined. These problems are described briefly in the report and are being partially resolved now that we are experiencing resumption of normal rainfall which unfortunately was also preceded by icing conditions that also interrupted column operations.

I appreciate your efforts in supporting the release of the supplemental project funds ($17,563) requested and recommended for approval last fall. We have depleted our budget resources to the point that it is difficult to maintain our research initiatives on this project. I am concerned that further delays will greatly reduce the overall value of our efforts which need particular attention now that wetter and warmer weather is imminent. Moreover, some time is needed to plan and schedule the resumption of associated analytical efforts and removal and analysis of the column contents. Since completion of these efforts even with a more timely receipt of this support is probably not possible by the present March 22, 1982 termination date of the project, an additional extension of the project period now appears inevitable. Therefore, I would request that the termination date of the project be extended to June 31, 1982 to permit better accommodation of the project objectives.

Your consideration and prompt attention to this matter is appreciated.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP/hb
enclosure

cc: Dr. J. E. Fitzgerald, CE
Ms. Faith Costello, OCA

Quarterly Progress Report No. 11

"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle"

EPA Grant No. R-806498
Research Project E-20-666

Georgia Institute of Technology
Atlanta, Georgia

October 1, 1981 - December 31, 1981

During this phase of the project, operation of the four simulated landfill columns was continued but on a curtailed frequency due to the lack of rainfall and corresponding production of sufficient leachate to enable leachate recycle on a daily basis. Although some additional tap water has been added, it was decided to cease recycle operations and re-commence them when more normal rainfall had resumed. This has led to an interruption in new sample acquisition and analysis during this period; the major effort therefore has been devoted to updating and completing analyses on previously acquired samples. These analyses, together with previously accumulated data, have formed the basis for preparation of a manuscript on "The Reactivity and Fate of Heavy Metals during Landfill Disposal of Solid and Hazardous Waste" to be presented at the Eighth Annual EPA Research Symposium on Land Disposal, Incineration and Treatment of Hazardous Waste scheduled for Cincinnati, Ohio March 8-10, 1982. A copy of this manuscript has been submitted to the sponsor.

Because much of the data analysis conducted during this report period has been included in the symposium presentation, it will not be repeated here. However, these data are being augmented by an additional investigation of the potential reactions explaining the behavior of the heavy metals in the leachate from the test columns. This analysis will be reported further at the end of the next project period and includes a special focus on equilibrium concepts with reference to the influence of activity and other complexing constituents on the mobility of the heavy metals transferred to the simulated landfill leachates. It is hoped that sufficient rainfall will have also occurred by that time to permit a resumption of regular leachate recycle and analysis.

Because of the delay in landfill stabilization incurred collectively by the unusually long dry weather period and the apparent inhibition of the biologically mediated processes within the test columns, it has become apparent that the anticipated completion of the project will be prolonged beyond the termination date of March 22, 1982. Therefore, it was deemed appropriate to delay the scheduled removal and analysis of the column contents until this stabilization could be better established. Moreover, the anticipated supplemental support requested in October 1981 to implement this latter activity has not materialized as yet and has necessitated an overall reduction in research personnel and effort.

These events have seriously hampered timely completion of the project by the proposed target date and suggest the need to extend this date for an additional period. Such an extension, coupled with receipt of earmarked funding, would provide for a more thorough and convincing documentation of the effects of heavy metals on landfill disposal of solid wastes. Therefore, during the next project phase, recycle will be continued and preparations for final removal and analysis of the column contents will be commenced if viable funding is available.

Frederick G. Pohland
Project Director

LIBRARY DOES NOT HAVE

Quarterly Progress Report No. 12, for the period of January 1, 1982 through March 31, 1982.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

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July 10, 1982

Mr. Mike Roulier, Project Manager
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

Re: R-806498, "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle". (E-20-666)

Dear Mike:

Enclosed find the thirteenth quarterly progress report for the subject project covering the period April 1, 1982 through June 30, 1982. You will note that the project is winding down and we are presently engaged in the completion of our analytical efforts and preparation of the final report. This report should be available by the September 22, 1982 project extension date and I presume that I will be receiving formal notification of approval of this amendment per your April 6, 1982 correspondence.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering

FGP/hb

cc: Dr. J. E. Fitzgerald, Jr., CE
Ms. Faith Costello, OCA

Quarterly Progress Report No. 13

"Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle

EPA Grant No. R-806598
Research Project E-20-666

Georgia Institute of Technology
Atlanta, Georgia

April 1, 1982 - June 30, 1982

During this quarterly project period, routine operation and sampling of all four simulated landfill columns was discontinued to provide an opportunity to update and complete the leachate analyses and to plan and schedule the eventual dismantling of the columns and retrieval of post-closure samples. Therefore, much of the effort during the ensuing quarter will be directed toward data compilation and evaluation prior to preparation of the final report. The samples acquired from each simulated landfill column will be subjected to the same analyses employed when the residential solid wastes and plating wastes were first placed in order to determine whether stabilization and/or reaction with time had significantly altered the concentrations of constituents. This comparison will also be used to ascertain the value of the various indicator parameters in making such an assessment.

It is anticipated that in the final analysis, the data will indicate sequences of operating conditions and environmental changes within the landfills and leachate with time. The apparent mobility/reactivity of the heavy metals and the ability of the landfill environment, established by codisposal of the municipal and industrial waste, to attenuate these concentrations will receive primary attention. Hence, the overall results should yield information regarding the efficacy of such a landfill management option in conventional practice as well as additional fortification for the leachate recycle concept in general.

The simulated landfill columns will be dismantled in sections to provide both visual inspection and uniform sampling for analysis to determine possible changes consequenced by the leachate/waste interactions prevailing during the experimental period. Each section will be composed of a lateral slice of the column contents, with three sections obtained for inspection and analysis per column. If informative, photographic records of these sections will also be obtained and included to augment the final report to be prepared during the next project period.

Frederick G. Pohland
Project Director

E-20-666B

Georgia Institute of Technology

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

ATLANTA, GEORGIA 30332

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TELEX: 542507 GTRC OCA ATL

TELEPHONE
(404) 894- 2265

March 16, 1987

Mr. Charles Moench
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Re: Final Report: "Fate of Heavy Metals During Landfill Stabilization of Solid Waste Materials with Leachate Recycle", R-806498 (E-20-666)

Dear Charles:

Enclosed find two copies of the Final Report for the subject research project which was originally submitted in draft form on August 1, 1984. I certainly appreciate your efforts in assisting Mike Roulier to complete the final processing of this report. Because some time has passed since we completed the work, I have carefully considered the review comments and have incorporated them into the revision according to prescribed format instructions.

You will note that revisions are marked in red on the draft copy included herewith, and that they embrace and respond to each of the several comments provided by the reviewers. I have also included a project summary for your consideration as requested.

I trust that the revised copy and project summary meet with approval. Please inform me of any action taken and when these documents will be available for general distribution. If you require any additional input, please contact me accordingly.

Best regards.

Sincerely,

Frederick G. Pohland
Professor of Civil Engineering
Project Director

FGP/hb
Enclosure
cc: Dr. Mike Roulier
Dr. J. E. Fitzgerald, C.E.
Mr. B. J. Lindberg, OCA
OCA Reports Coordinator

PROJECT SUMMARY

FATE OF HEAVY METALS DURING LANDFILL STABILIZATION OF SOLID WASTE MATERIALS WITH LEACHATE RECYCLE

Frederick G. Pohland, Joseph P. Gould,
Winston R. Esteves and Bruce J. Spiller

The research reported herein was initiated at the Georgia Institute of Technology in September 1979 with support from the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH to provide an evaluation of the fate and effect of heavy metals codisposed with refuse in municipal landfills. Accordingly, four simulated landfill columns were constructed and loaded with municipal refuse alone or in combination with three levels of alkaline heavy metal plating treatment sludges. Each column was covered with a final layer of soil, received incident rainfall and was operated with leachate collection and recycle. Parametric analyses on the waste and leachate were conducted over an operational period of about two years.

INTRODUCTION

Enactment of the Resource Conservation and Recovery Act (RCRA) of 1976 and Hazardous Solid Waste Amendments of 1984, publication of guidelines and regulations governing the handling of hazardous materials from generation to ultimate disposal, and current concern over the nature and fate of pollutants released to the environment have increased focus and attention on the control and operation of land disposal sites receiving both solid and hazardous wastes. In the case of hazardous wastes, current regulations require maximum containment with control of migration of leachate and gas into the environment.

Unfortunately, it has been traditional throughout the United States to discard many hazardous wastes by simple codisposal with other materials, often in landfills originally conceived and eventually operated as disposal sites for municipal refuse. Even in those circumstances where segregation has been attempted, the usual procedure has been to bury and hope that the land will be a sufficient and ultimately satisfactory environmental receptor. This approach continues to prevail at many municipal landfills receiving small but continuous increments of hazardous wastes. Procedures such as these have led to numerous cases of environmental impairment, due primarily to excursions of leached materials into the surface and ground waters adjacent to the landfill site. Although such excursions are being better documented and remedial control actions more frequently imposed, many uncertainties still remain regarding the ultimate fate of hazardous materials subjected to such land disposal practices.

This research initiative was conceived in recognition of a need to more comprehensively examine the consequences of codisposal of municipal and hazardous wastes. Therefore, the primary goal was to investigate landfill behavior and the associated relative and ultimate potential for environmental impairment by heavy metals when codisposed with municipal refuse in a landfill site. An alkaline metal plating treatment sludge containing primarily chromium, cadmium, nickel and zinc was selected and placed in varying quantities with municipal refuse in a series of simulated landfill columns operated under the influence of leachate containment, collection and recycle. The unique feature of this study was the assessment of potential migration of the heavy metals during microbially mediated stabilization of the readily decomposable organic fractions of municipal refuse when accelerated by leachate recycle. Detailed analyses of leachate characteristics were included and used to define and interpret landfill behavior, the relative impacts of the heavy metal sludge on this behavior, and the potential for attenuation and/or release of heavy metals under a range of refuse to hazardous waste sludge loading ratios.

MATERIALS AND METHODS

The four simulated landfill columns were operationally similar to those illustrated in Figure 1. One column served as the control and contained no metal sludge additions, whereas the other three test columns contained bulk municipal refuse and increasing loadings of heavy metal sludge in accordance with the information presented in Table 1.

TABLE 1. CHARACTERISTICS AND LOADINGS OF HEAVY METAL SLUDGE CODISPOSED WITH MUNICIPAL REFUSE IN SIMULATED LANDFILL COLUMNS

Sludge Characteristics	Analysis
Moisture Content, %	84.7
Volatile Solids, % dry	24.6
Zinc, mg/kg dry	317,000
Chromium, mg/kg dry	21,000
Nickel, mg/kg dry	400
Cadmium, mg/kg dry	13,100
Copper, mg/kg dry	185
Iron, mg/kg dry	94,000

Column Loadings: Column 1; 400 kg bulk refuse, 37.3 kg bulk sawdust
Column 2; 400 kg bulk refuse, 37.3 kg bulk sawdust, 33.6 kg sludge
Column 3; 400 kg bulk refuse, 37.3 kg bulk sawdust, 65.8 kg sludge
Column 4; 400 kg bulk refuse, 37.3 kg bulk sawdust, 135.2 kg sludge

Since the objectives of the studies were to assess the extent to which heavy metals might be assimilated during codisposal with municipal refuse and to ascertain the impact of the admixed metal sludges on the normal progress of landfill stabilization, the metal levels in the leachates from the four simulated landfill columns were carefully monitored together with a broad array of routine indicator parameters. In order to simplify the analysis of these data, the project period was divided into five operational phases based upon the observed events that occurred as stabilization progressed. Accordingly, the operating history generally could be described according to the operational periods and associated characteristics indicated in Table 2.

TABLE 2. PHASES OF SIMULATED LANDFILL OPERATIONS

Experimental Phase	Days	Operational Characteristics
A	0-200	Washout and/or facile production of leachate
B	200-380	Initial microbially mediated stabilization
B'	380-480	No leachate production or recycle; period of drought
C	480-600	Post-drought resumption of leachate production
D	600-720	Terminal phase of leachate production

RESULTS AND DISCUSSION

To appropriately determine the influence of the heavy metal loadings on the progress of landfill stabilization and the capacity of the landfill environment to assimilate heavy metals, leachate heavy metal content was recorded with time and experimental phase. Since zinc was one of the major constituents in the heavy metal sludge, leachate zinc mass concentrations are presented in Figure 2 as representative of heavy metal behavior. A data gap between Phases B and C occurred as the period of drought eliminated rainfall induced leachate production.

Fluctuations in zinc (as well as the other heavy metals) followed a pattern responsive to chemical reactivity and the sludge loading intensities of the test columns. Whereas, the control column exhibited little detectable zinc, there was an initial washout and fixation of readily soluble metals from the sludge, followed by a period of relative stability leading up to the cessation of leachate production during the drought. This relatively stable mass concentration was maintained for a considerable period following resumption of leachate production, with eventual increasing amounts being generated toward the termination of the investigations, particularly for the most heavily loaded columns. A similar pattern was established for cadmium (Figure 3), although mass concentrations in the leachate were of lower magnitude.

The most striking feature of these results was the apparent ability of the columns without or with the lowest heavy metal loading to exhibit a lasting assimilative capacity for heavy metals. Comparisons of the data from Columns 1 and 2 with those of Columns 3 and 4 indicate definite immobilization of zinc and cadimum in the case of the former two columns as opposed to significantly increased mobility of these metals in the leachates from the latter two columns. Therefore, these heavy metal loadings to Column 2 were sufficiently low to permit microbially mediated assimilation, whereas those for Columns 3 and 4 overwhelmed this process. Once the assimilative capacity was exhausted, heavy metals increased in the leachates in accordance with prevailing solubility equilibria.

The preceding observation was further reinforced by data descriptive of the conversion and removal of organic waste constituents transferred to the leachate medium. Using chemical oxygen demand (COD) as an indicator of the total organic content of the leachate, the data in Figure 4 again suggest that leachate COD was removed by microbially mediated conversion of total volatile acid intermediates as landfill stabilization progressed in Columns 1 and 2. In contrast, such conversion was not evident for Columns 3 and 4, thereby lending credence to the likelihood of heavy metal inhibition. Indeed, the increase in COD as the experiments progressed suggested not only the accumulation of biologically degradable intermediates in the leachates from these more heavily sludge loaded columns, but the formation of more refractory conversion products including the humic-like substances.

The data of Figures 2 through 4 indicate that heavy metal loadings can either inhibit or retard microbially mediated conversion of waste organic materials, but that given time for acclimation as was apparently provided during the drought period in Column 2, certain loadings of heavy metals can also be assimilated. The extent of loading would necessarily be a function of the nature of the sludge, the manner in which it was codisposed in the landfill setting, and the potential for reaction within the landfill environment in terms of solubility and precipitation or complexation.

In most landfill environments, the most important single solubility control for the toxic heavy metals studied in this investigation is the availability of sulfide produced by reduction of sulfates. The pH conditions and presence of sulfides for this purpose confirmed this premise. However, on the basis of a detailed consideration of solubility and acid-base equilibria calculations, corrected for activity changes due to high leachate ionic strengths, it was determined that while leachate heavy metal concentrations were too low to be controlled by such potential precipitating anions as hydroxide or carbonate, the concentrations were significantly higher than could be reasonably accounted for by reference to the measured levels of leachate sulfide.

In consideration of this apparent contradiction, it was concluded that some other leachate component was increasing heavy metal mobility above those predictable by solubility considerations, particularly toward the later portion of the experimental investigations. The recorded increase in leachate COD during this time implicated the humic-like substances as possible complexing agents for heavy metals. Based upon what is known about their origin and structure, the aromatic hydroxyl (ArOH) or phenolic compounds served as a sufficient measurement of mass concentration throughout the phases of the studies as indicated in Figure 5. Moreover, because these substances are considered significant complexing agents for the transition metals loaded to the test columns, the impact of their effect on heavy metal mobility could be evaluated by inspecting the relationship of the leachate heavy metals and the aromatic hydroxyl concentrations.

Using zinc as a representative heavy metal, the relationship between it and the ArOH concentrations is illustrated in Figure 6 for the leachate samples from the three test columns throughout the entire experimental period. The positive correlation, observed also for cadmium and nickel, confirmed the role of the humic-like substances in affecting heavy metal mobility. Therefore, within the landfill perspective, it could be postulated that the particles of alkaline metal hydroxide sludge codisposed with the municipal refuse reacted with the leachate to solubilize and then precipitate or complex heavy metals, possibly in a sequential manner with concomitant encapsulation of the sludge by sulfide upon reduction of its sulfate content in the anaerobic reducing environment of the columns. Thereafter, the further release of heavy metals was directed by the opportunity for interaction between the sulfides and high molecular weight humic-like substances.

This later release and increased mobility of complexed heavy metals, although less available to exert direct inhibitory effects, may be cause for concern in terms of potential for long-term leaching and migration from the landfill mass. Therefore, judicious selection of loading levels and techniques as well as eventual removal of the leachate transport medium prior to production of humic-like substances after the readily available waste organic constituents have been exhausted would be indicated as an important operational strategy. This strategy could be easily accommodated with containment and recycle systems by removing the leachate with its component nutrients and capping the site to preclude or minimize further influx of moisture and resultant leachate formation.

CONCLUSIONS

The results of the landfill codisposal investigations provided a clear determination of the assimilative capacity for admixed heavy metal sludges. Heavy metal sludge loadings of 0.077 kg/kg of bulk municipal refuse were effectively assimilated. At a sludge loading that did not exceed this ratio, the characteristics of the leachate from the sludge-bearing column was indistinguishable from those of the sludge-free column with little evidence of lasting inhibition of the microbially mediated processes of waste stabilization. At higher loadings, inhibitory effects were clearly evident and a ratio of 0.15 kg of sludge per kg of bulk refuse inhibited stabilization which proceeded only into the acid formation phase.

Precipitation of heavy metals and/or encapsulation of the originally added alkaline hydroxide sludge by a protective layer of sparingly soluble sulfides and carbonates provided major attenuation mechanisms, while aromatic hydroxyl compounds acted to mobilize heavy metals through complexation.

Improved contact between the leachate and solid matrix afforded by leachate recycle decreased the variability of indicator parameters and enhanced the attainment of equilibrium conditions with respect to _in situ_ chemical and biological processes. This provided a better opportunity to ascertain both the loading levels and techniques requisite to permit attenuation without inhibition of the progress of landfill stabilization. To better establish the range of loadings capable of being accommodated at landfill disposal sites, additional studies with varying quantities and types of hazardous wastes codisposed with municipal refuse are considered warranted.

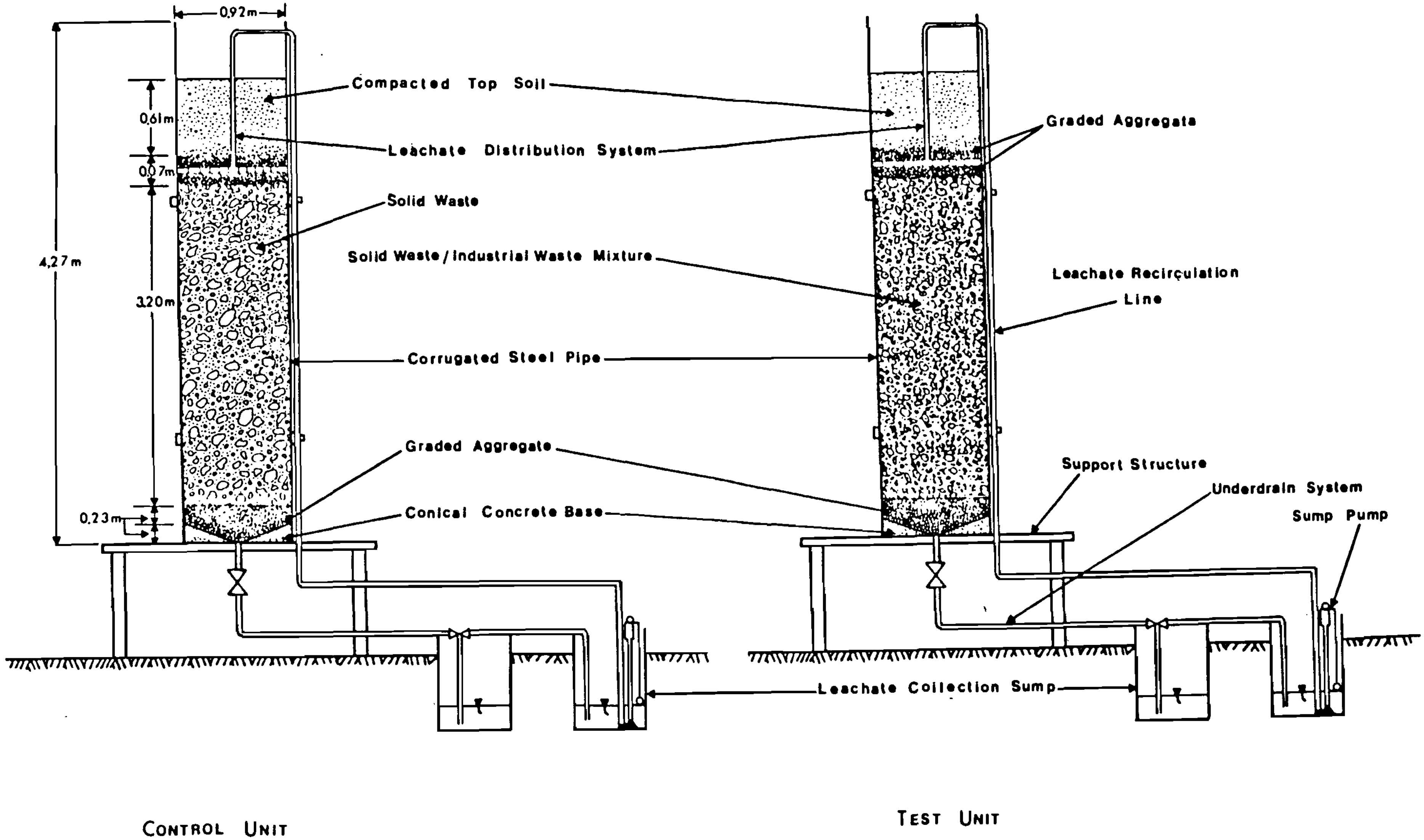

Figure 1. Simulated Landfill Columns with Leachate Collection and Recycle

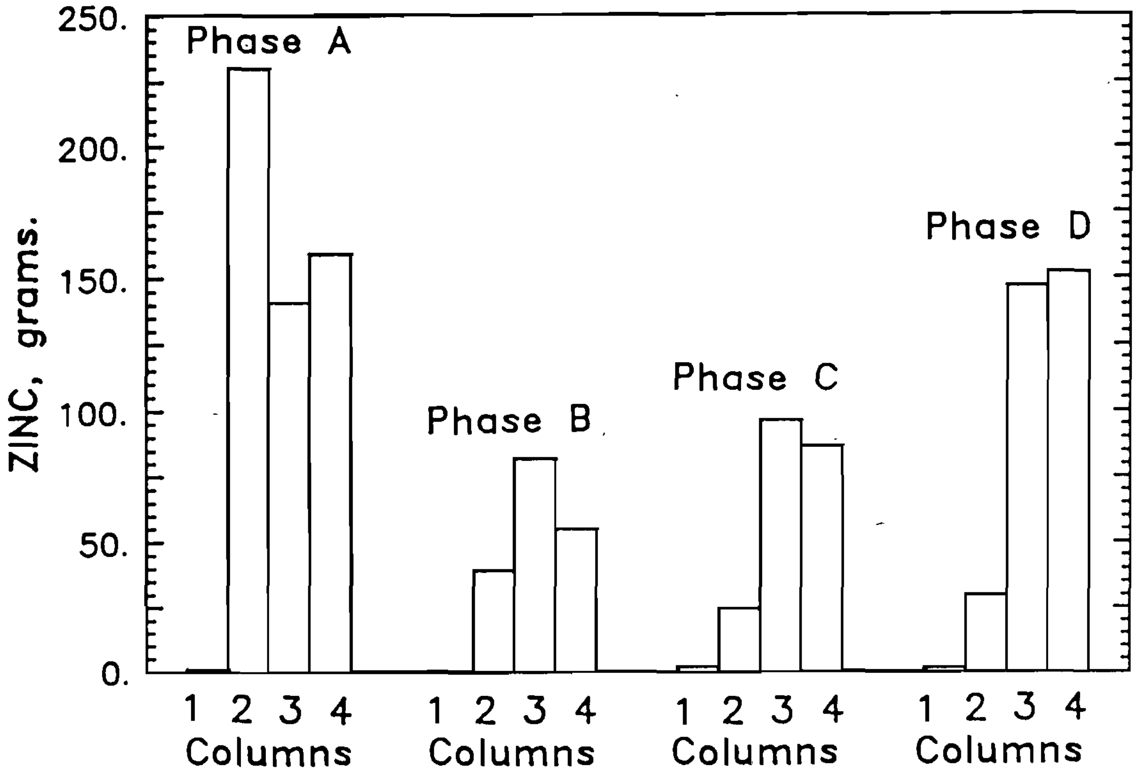

Figure 2. Average Content of Zinc During Experimental Phases

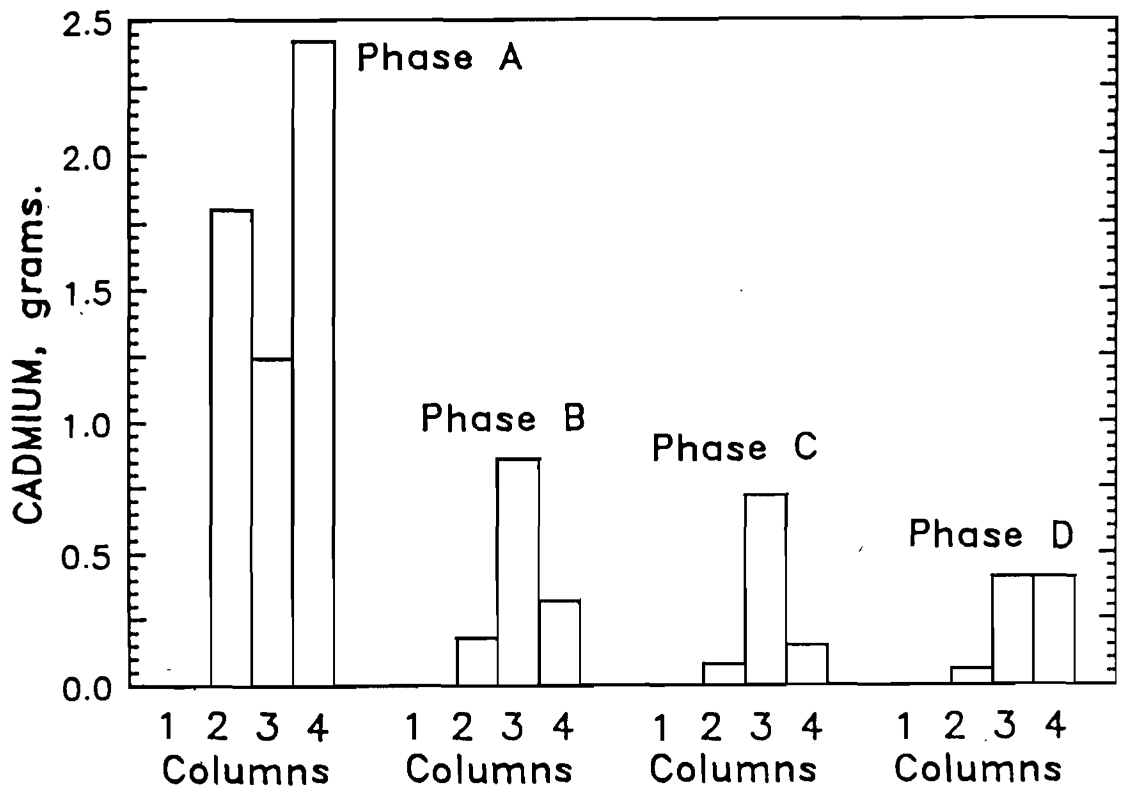

Figure 3. Average Content of Cadmium During Experimental Phases

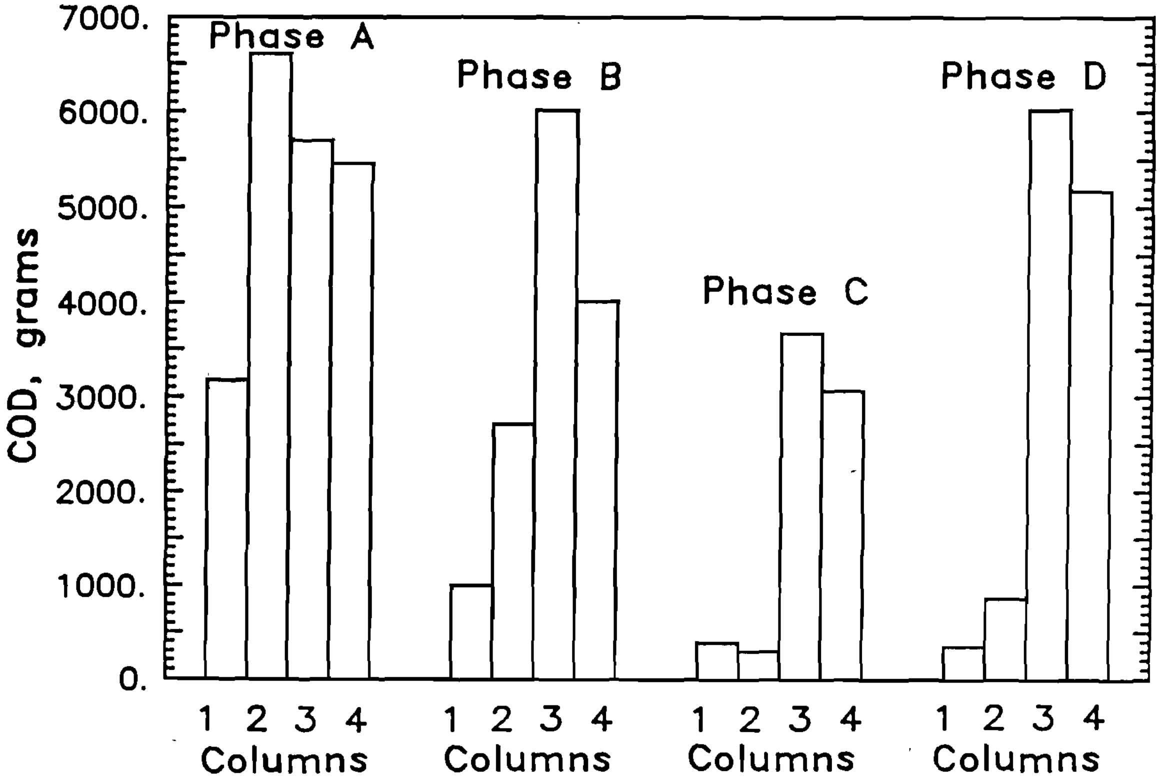

Figure 4. Average Chemical Oxygen Demand During Experimental Phases

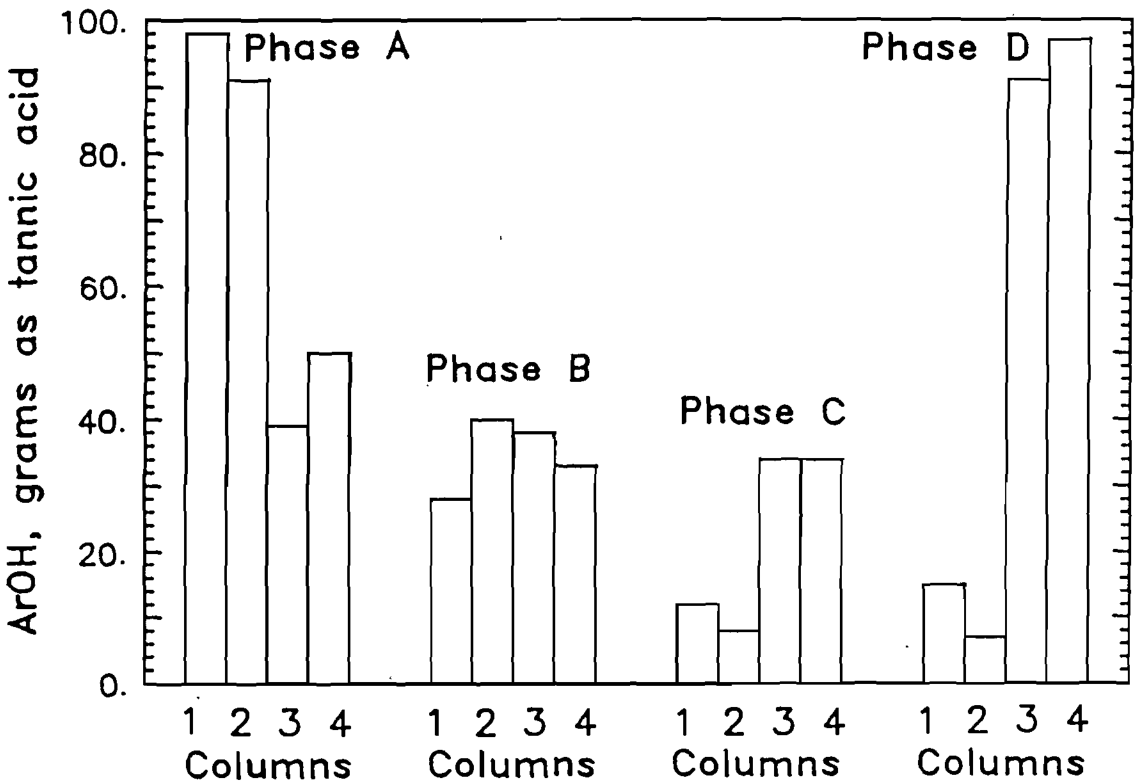

Figure 5. Average Content of Aromatic Hydroxyl During Experimental Phases

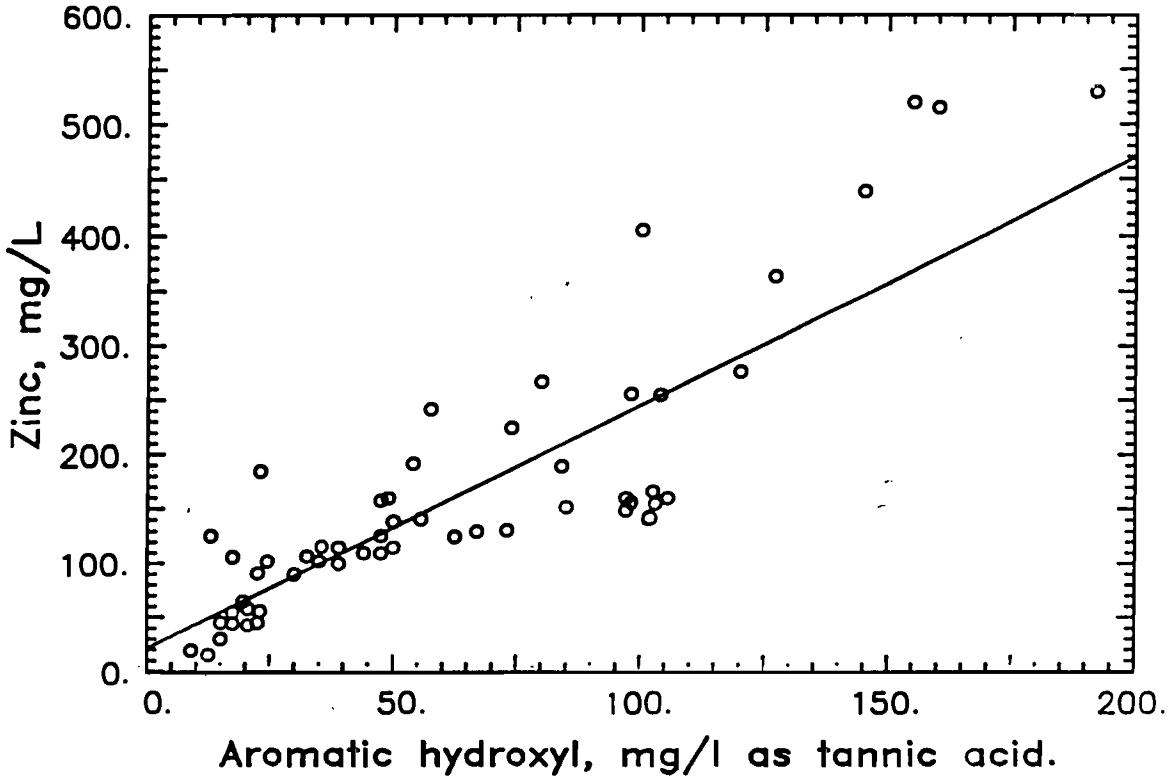

Figure 6. Zinc Concentration Versus Aromatic Hydroxyl Concentration

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FATE OF HEAVY METALS DURING LANDFILL STABILIZATION OF SOLID WASTE MATERIALS WITH LEACHATE RECYCLE

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NOTICE

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Resarch Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report documents the results of a 3-year research initiative dealing with the effects of codisposal of industrial metal plating treatment sludge with municipal refuse. The investigations were conducted in four simulated landfill columns operated with leachate collection and recycle. One column served as a control without sludge additions; the other three test columns received increasing loadings of heavy metal sludges. Detailed analyses on changes in leachate characteristics between the control and test columns provided insights into the heavy metal loadings capable of being assimilated during the normal progress of microbially mediated refuse stabilization without imparting inhibition or a potential for release of heavy metals and adverse environmental impacts.

For further information, please contact the authors or the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

ABSTRACT

The research reported herein was initiated at the Georgia Institute of Technology in September 1979 with support from the U.S. Environmental Protection Agency, Cincinnati, OH to provide an evaluation of the fate and effect of heavy metals codisposed with refuse in municipal landfills. Accordingly, four simulated landfill columns were constructed and operated with leachate collection and recycle. The results of leachate analyses from a control column containing only bulk municipal refuse were compared with those from three test columns containing municipal refuse and increasing loadings of alkaline heavy metal plating treatment sludge. Each column was covered with a final layer of soil and received incident rainfall throughout a 2-year project period. Parametric analyses on waste and leachate composition indicated that heavy metal loadings could be either assimilated by or exhibit an inhibitory influence on the *in situ* microbially mediated processes of landfill stabilization. Mechanisms of assimilation are suggested together with landfill management procedures applicable to such codisposal operations.

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SECTION 1

INTRODUCTION

The enactment of the Resource Conservation and Recovery Act (RCRA) of 1976 and the Hazardous and Solid Waste Amendments of 1984 have resulted in publication of guidelines and regulations governing the handling of hazardous materials from generation to disposal. In addition, increasing concern over the nature and fate of pollutants released to the environment has led to new initiatives for their control at land disposal sites by both the regulatory and industrial sectors. In the case of hazardous wastes, current regulations require maximum site containment and control of migration of leachate and gas into the surrounding environment. Most of this waste is generated by industrial activities; total contributions of industrial wastes slated for landfill disposal have been estimated to approach 300 million dry tons during this decade (Gorden, 1975). Current estimates also indicate that about 10-15 percent of these wastes will be classified as hazardous and, if those from households or small quantity generators (<100 kg/month) were included, this total quantity could be considerably increased.

Unfortunately, it has been traditional throughout the United States to discard many hazardous wastes by simple codisposal with other materials, often in landfills originally conceived and eventually operated as disposal sites for municipal refuse. Even in those circumstances where segregation has been attempted, the usual procedure has been to bury and hope that the land will be a sufficient and ultimately satisfactory environmental receptor. This approach continues to prevail at many municipal landfills receiving small but continuous increments of hazardous wastes. Procedures such as these have led to numerous cases of environmental impairment, due primarily to excursions of leached materials into the surface and ground waters adjacent to landfill sites. Although such excursions are being better documented and remedial control actions more frequently imposed, many uncertainties still remain regarding the ultimate fate of hazardous materials subjected to such land disposal practices.

This research initiative was conceived in recognition of a need to examine more comprehensively the issue of codisposal of municipal and hazardous wastes. Therefore, the primary goal was to investigate landfill behavior and the associated relative and ultimate potential for environmental impairment by heavy metals in hazardous wastes when codisposed with municipal refuse in a landfill site. A metal processing waste sludge containing primarily chromium, cadmium, nickel and zinc was selected and placed in varying quantities with municipal refuse in a series of simulated landfills operated under the influence of leachate containment, collection and recycle. The unique feature of this study was the assessment of potential migration of the heavy metals during the sequences of events reponsible for microbially mediated stabilization of the readily decomposed organic fractions of municipal refuse when accelerated by leachate capture and recycle within the simulated landfills. Detailed analyses of leachate characteristics were included and used to define and interpret landfill behavior, the relative impacts of the heavy metal sludge on this behavior, and the potential for attenuation and/or release of heavy metals under a range of refuse to hazardous waste sludge ratios.

SECTION 2

SUMMARY AND CONCLUSIONS

Experimental landfill lysimeter columns operated with leachate recycle and containing 400 kg of bulk municipal refuse with various levels of admixed heavy metal sludges demonstrated systematic responses to the sludge loadings. Based on careful consideration of potential inhibition by the heavy metal sludge, the test columns (Nos. 2, 3 and 4) received admixed loadings 33.6, 65.8 and 135.2 kg of sludge, respectively. In general, leachate characteristics for the sludge-free control column (No. 1) and Column 2 with the lowest sludge loading were very similar and essentially indistinguishable for most parameters, thereby indicating that the 33.6-kg sludge loading did not exceed the microbially mediated assimilative capacity of the system. In contrast, the leachates from Columns 3 and 4 showed evidence of severe microbial inhibition, thereby indicating that these higher sludge loadings overtaxed the attenuation mechanisms available.

The addition of metal sludges to the lysimeters had the effect of increasing the concentrations of metals (Zn, Cd and Ni) in the leachate. Following an early period of metal washout during which rapid metal mobilization was reflected in high leachate metal concentrations, a balance between processes of metal fixation and mobilization led to reduced and reasonably stable levels of heavy metal in the leachate. The experimental evidence from these studies indicates that leachate recycle, by affording increased contact between the sludge solids and leachate, accelerated stabilization with an associated rapid decrease in heavy metal levels following the initial washout phase. In addition, the stabilizing effect of recycle tended to reduce the random daily variations in leachate metal concentrations. Such increased stability would enhance process predictability and the options for management of leachates at codisposal sites.

The impact of leachate recycle on landfill management was demonstrated in several ways. In particular, intimate contact between the leachate and heavy metal sludge/refuse mixture enhanced homogeneity and encouraged reaction between the sludge particle surfaces and dissolved species in the leachate. The evidence supporting this premise included:

a. Aromatic hydroxyl (ArOH) levels in the leachate diminished in proportion to the metal sludge content originally placed in the columns, strongly suggesting that the ArOH was being bound by chemical interactions with the solid surface;

b. Inorganic carbon levels, i.e., carbonates in the leachate, decreased as the sludge loadings increased. Since metal carbonates are generally of lower solubility than the corresponding metal hydroxides, this systematic decrease in carbonate concentrations was ascribed to the exchange of carbonate for hydroxide at the metal hydroxide sludge surface and had the effect of encapsulating the sludge particles in a layer of relatively sparingly soluble metal carbonates;

c. In spite of the usual presence of reducing conditions in the simulated landfills, and availability of abundant reducible sulfates, the total sulfide concentrations in the leachates were surprisingly low. While this may have been partially accounted for by precipitation of metal sufides, it was probable that interactions between the sulfides and metals in the sludges also affected sulfide removal. Such an interaction would result in the conversion of solid metal hydroxides and carbonates into even less soluble metal sulfides with the formation of a protective surface layer. Although the column design and operation did not permit eventual isolation of sufficient sludge samples following completion of the column operations to conduct a detailed analysis, a visual examination of sludge particles, conducted under low power (10X) magnification, indicated a very obvious uniform blackening of these particles. This black coating is consistent with the formation and deposition of a metal sulfide layer around the sludge particles;

d. There was some indication that phosphates were being removed from the leachates by other than biological processes. The obvious removal candidate for phosphates was the sludge, since it contained high levels of calcium as well as other metals which are capable of forming sparingly soluble phosphate complexes; and,

e. Levels of dissolved ionic substances, determined by conductivity measurements in the leachates from the three sludge-laden columns (Nos. 2, 3 and 4), were substantially higher than those in the control column (No. 1) during the initial phases of operation and decreased to levels approximately equal to those of the control column by the termination of the study. This indicated that otherwise easily mobilized sludge components had been protected, possibly by encapsulation, from transfer to the leachate.

The combined experimental evidence strongly indicated an interaction between the hydroxide particles of the sludge with the soluble leachate constituents. The net effect of such a process was the encapsulation of the sludge particles in a protective layer of very sparingly soluble sulfides and carbonates which markedly reduced the availability of these metals for leaching. Moreover, this beneficial encapsulation will be enhanced by limited distribution of the codisposed sludge and by intimate contact between the leachate and sludge solids. This contact is promoted by leachate recycle, thereby resulting in a markedly reduced toxic metal mobility.

The response of the simulated landfill columns to the addition of heavy metal sludge demonstrated clearly that, while such sludges could have a distinct inhibitory impact on microbially mediated stabilization, the landfills displayed a significant ability to withstand this impact below a certain level of sludge addition. As long as the added levels of metal sludge were below the microbially mediated assimilative capacity, chemical and biological mechanisms within the landfills were sufficient to compensate for the toxic or inhibitory influences of the heavy metals. The evidence for this assimilatory capacity was clearly demonstrated by the results of leachate analyses for Column 2 where 33.6 kg of heavy metal sludge had virtually indistinguishable effects on the organic parameters examined (COD, BOD_5, TVA, ArOH) when compared with the leachate analyses for Column 1, the sludge-free control column. Columns 3 and 4, containing 65.8 and 135.1 kg of sludge, respectively, revealed leachate characteristics essentially identical to each other but quite distinct from Columns 1 and 2 leachates. These more heavily loaded columns displayed strong evidence of toxicity or inhibition with respect to these same leachate parameters. In addition, there were limited indications that a cyclic behavior was developing in these latter two columns with apparent periods of high toxicity/inhibition alternating with periods of lowered inhibition during which assimilative processes were partially compensating for the impact of the metal sludges.

Another very important observation with respect to leachate heavy metal mobilities was the strong positive correlation between levels of dissolved zinc, cadmium and nickel and the level of aromatic hydroxyl in the leachates. This correlation was ascribed to the formation of metal-humic substance complexes with consequent mobilization of the metals, possibly enhanced when readily biologically degradable substrates had been exhausted toward the end of the experimental investigations, particularly when inhibition was less or absent. Although such complexation will have the effect of increasing metal solubility, the metal- humic complexes may be substantially less toxic than the metal alone. Thus, the increased heavy metal mobility may not be associated with a corresponding increase in toxic or inhibitory effects.

When considered collectively, the results from the investigations of landfill codisposal of heavy metal sludges with municipal refuse suggested the following assimilative mechanisms:

a. Sulfide precipitation and immobilization;

b. Encapsulation of metal hydroxide sludge particles by carbonate and sulfide solids; and,

c. Formation of metal complexes with humic substances.

To the extent that these assimilative mechanisms will be enhanced by prolonged intimate contact between the leachate and the landfill mass, recycle will have a significant beneficial impact on the behavior of landfills containing heavy metal sludges. Indeed, recycle as practiced in these studies yielded sufficient contact between leachate and heavy metal solids to provide excellent correspondance between dissolved metal concentrations and predictions otherwise based on equilibrium considerations.

In summary, it has been demonstrated that:

1. Simulated landfill lysimeter columns operated with leachate recycle provided a clear determination of assimilative capacity for admixed heavy metal sludges. Heavy metal sludge loadings were effectively accommodated when codisposed in the ratio of 0.077 kg of sludge per kg of admixed bulk municipal refuse. At a sludge level which did not exceed this ratio, the charactristics of the leachate from the sludge-bearing column was indistinguishable from those of the sludge-free control column with little evidence of inhibition of the microbially mediated processes of waste stabilization. At higher levels of sludge addition, inhibitory effects were clearly established; a ratio of 0.15 kg of sludge per kg of refuse strongly inhibited microbially mediated conversion of available substrate and stabilization proceeded only into the acid formation phase.

2. Encapsulation of the originally added metal hydroxide sludge by a protective layer of sparingly soluble sulfides and carbonates provided a major attenuation mechanism, while aromatic hydroxyl species acted to mobilize heavy metals through the mechanism of complexation.

3. Enhanced contact of leachate with the solids matrix had the effect of decreasing the variability of leachate parameters and accelerating the attainment of equilibrium conditions with respect to in situ chemical and biological processes. Inhibition by the heavy metals content of the admixed sludges can be potentially nullified and allow for normal landfill stabilization to proceed with environmental minimal adverse consequences. The net effect of understanding the complexity and interrelationship between these processes can lead to more judicious landfill design, and control strategies.

4. Additional studies comparing landfill systems operated with leachate containment, collection and recycle, and with varying loadings and admix methods for types of hazardous waste materials, are warranted in order to further reveal the nature and/or efficacy of such codisposal practices at both existing and possible future landfill sites.

SECTION 3

LITERATURE REVIEW

Pertinent aspects of landfill disposal practices are presented in this review. Included are a description of the elements and processes associated with landfill stabilization, the analytical parameters indicative of the progress of stabilization, and selected results from other research on codisposal. Collectively, these components of the review were used to provide a basis for the research rationale and to fortify the final interpretation and significance of the experimental results.

LANDFILL STABILIZATION

Landfill stabilization may be considered the process of concomitant and/or sequential physical and chemical changes occurring during the life of a site. These changes may be rapid or slow, obvious or obscure, short-term or long-term, and mediated by a variety of natural and imposed conditions. Moreover, they may be detected and measured or controlled by a variety of techniques which provide the basic ingredients for understanding or developing a management strategy at any particular landfill site. The most obvious media in which to impose these measurement techniques are the leachate and gas produced and released throughout the progress of landfill stabilization. These, in turn, are dramatically influenced by the nature of wastes originally deposited, the origin and magnitude of moisture content (the major transport phase within the landfill), and the method of landfill operation and management.

Municipal Solid Waste Characteristics

The waste materials deposited in any landfill will vary not only in terms of source, but also in accordance with collection and disposal techniques. Accordingly, wastes may be derived from separate or combined residential, commercial, industrial and agricultural sources and may reach the disposal destination in bulk or processed condition, i.e., segregated, mixed, baled or shredded. This combination of wastes then may be subjected to various degrees of initial or final compaction, all of which will influence the overall rate and degree of stablization.

Several authors (Kaiser, 1966; Golueke and McGauhey, 1970; EMCON, 1975; Eiffert and Schwartzbaugh, 1977; Tchobanoglous, 1977) have reported the composition of municipal refuse; a compilation of these data is provided in Table 1. It is important to note that, while there exist certain degrees of variability from source to source and also from season to season, there is some consistency in the overall average contributions in terms of constituents

TABLE 1. RANGES OF COMPOSITION OF MUNICIPAL REFUSE

Refuse Component	Composition, % (1)*	(2)*	(3)*		(4)		(5)	
	Average	Average	Range	Average	Range	Average	Range	Typical
Food Wastes	12		8.8-12.8	10.7	4-9	7	6-26	15
		25.1						
Garden Wastes	-		5.8-17.0	10.4	1-10	5	0-20	12
Paper	39	44.5			45-57	50	25-45	40
			35.2-45.3	40.6				
Cardboard	7				-	-	3-15	4
Plastics	-				-	-	2-8	3
		2.2	4.2-5.2	4.6	-	-		
Rubber	2				4-9	6	0-2	1
Leather	-	-	-	-	-	-	0-2	1
Textiles	3	1.1	1.1-2.5	1.7	2-5	3	0-4	2
Plastic Film	2	-	-	-	-	-	-	-
Wood	7	-	0.4-1.3	1.0	1-2	1	1-4	2
Glass	10	11.3	9.1-12.4	10.9	9-17	12	4-16	8
Metals	8	8.7	8.0-8.6	9.0	6-15	10	-	-
Tin Cans	-	-	-	-	-	-	2-8	6
Non-ferrous Metals	-	-	-	-	-	-	0-1	1
Ferrous Metals	-	-	-	-	-	-	1-4	2
Dirt, Ashes, Brick, etc.	10	7.1	1.0-3.6	2.8	3-15	7	0-10	4
Moisture	-	-	-	-	21-35	27	15-40	20

(1) Kaiser, 1966
(2) Golueke, 1970
(3) EMCON, 1975
(4) Eiffert and Swartzbaugh, 1977
(5) Tchobanoglous, *et al.*, 1977

*Determined on an as received basis.

by category. Of more importance to the progress of stabilization, however, is the magnitude of the readily decomposable fraction represented mainly by food and garden wastes and other similarly organic-type components. As will be discussed later, these latter components contribute either directly or indirectly to leachate and gas characteristics as they are converted during landfill stabilization.

With regard to processing prior to landfill disposal of municipal refuse, Hentrich, et al. (1979) indicated that baling of refuse prior to disposal enhanced both the rate of leachate production as well as the volume of leachate produced, although the organic leachate constituents were of lower strength than from landfills without refuse processing. In the same study it was also shown that waste shredding prior to disposal retarded both the rate of production and the final volume of leachate produced. However, the leachate was of a significantly higher organic strength than leachate from a baling operation or from an unprocessed refuse. Use of both shredding and baling prior to final disposal was inconclusive with regard to leachate characteristics, probably indicating compensating influences.

Particle size reduction by refuse shredding could be expected to increase the opportunity for microbial utilization and conversion by increasing surface area available for both moisture retention and leaching as well as substrate availability (DeWalle, et al. 1977; Fungaroli and Steiner, 1979). However, uncertainty remains regarding the explicit influence of this pretreatment conditioning; Buivid (1980) indicated a decrease in waste conversion rates.

Since it is difficult to control the composition of municipal refuse received at a landfill site, particularly if the commercial and industrial sectors are complex and not otherwise regulated, the impact of toxic and hazardous waste inputs is also difficult to ascertain. As will be demonstrated later in this review, little information is available on the results of codisposal of industrial wastes with municipal refuse, since site specific analytical data are usually lacking. Hence, landfills that were originally conceived and eventually operated as sanitary landfills often have received hazardous wastes at some time during their operational life with little attention given to the ramifications of such inputs, perhaps because they were not immediately apparent. Studies, such as reported herein, are needed to focus on the issue of superimposing hazardous waste materials on the municipal landfill setting.

Moisture Content

The amount of liquid present within a landfill site is of crucial importance to the understanding and control of the inherent processes of stabilization, since it serves as the principal transport medium and stimulates the formation of leachate and gas. Therefore, a sufficient description of the local hydrometeorology and hydrogeology is required to anticipate both the potential for infiltration and exfiltration into and out of the site. Moreover, this information must be interpreted within an anticipated operational perspective, viz., type and character of the refuse, possibility of prior processing, and landfill design and operational features, particularly with respect to the possible use of leachate and gas control and treatment systems.

If a landfill site is not to be lined for containment, an understanding of groundwater and contaminant movement is necessary for proper determination of design acceptability during both construction and operational phases. This analysis preferably should be performed in three dimensions to avoid erroneous prediction in both time and space. In humid regions, ground water occupies all the openings in the earth materials below the top of the zone of saturation or the water table. Above the water table, these openings are only partially filled with water and rain or other liquids may penetrate downward to the zone of saturation and become part of the groundwater reservoir. These waters may be contaminated through direct flow and by diffusion/dispersion if continuity exists with the landfill site and leaching is permitted to occur.

Hydrogeologic studies at four sites in northeastern Illinois have indicated that approximately one-half of the annual precipitation infiltrated into the landfills (Hughes, et al., 1971). Moreover, groundwater levels below the sites tended to rise to form groundwater mounds which, if sufficient to intersect the ground surface, resulted in leachate springs and seeps. Leachate may also drain directly into the ground water or move laterally, often to outcrop in depressions or into surface water resources. This movement is generally random and influenced by the geological setting and its textural and structural characteristics.

Regardless of origin, if given opportunity for contact with the refuse constituents in a landfill, the accumulated liquid will determine the amount and character of the leachate formed in both temporal and spacial dimensions. Leachate production probably begins with refuse placement in the site, but is not actually perceived until the point at which the refuse has become saturated and further influx of moisture delivers an equal quantity of liquid migration from the site. Predictions on the amount of leachate that can be produced at any landfill have been approached by providing a water balance around the landfill, usually based on the relationships between precipitation, evaporation, transpiration, surface runoff and underflow (Streng and Jackson, 1976). Until field capacity or leachate excess is reached, the moisture available is regarded as being a balance between those quantities that enter as precipitation and leave through evaporation. By applying the principle of continuity, leachate generation is then equated to percolation plus underflow, where percolation would be the sum of precipitation and runoff into the landfill minus evapotranspiration and runoff from the landfill. Therefore, climate dramatically influences the temporal nature of leachate generation and quality at a landfill location.

In the initial stages of landfill development, there is rarely adequate moisture available (Table 1) to stimulate the physical and biochemical processes leading to the formation of leachate and gas. With regard to the latter, 25 percent moisture is the generally accepted minimum for microbially mediated decomposition to commence, and levels of only 30 to 40 percent moisture content have been reported to curtail methane production (Streng and Jackson, 1976). Maximum gas production has been observed at moisture contents ranging from 60 to 80 percent by weight of refuse in studies intended to maximize gas production but minimize the production of excess leachate (Walsh and Kinman, 1979). The potential of ground and surface water contamination by leachate has been a major restriction to intentional moisture addition to landfills to enhance the onset and intensity of gas production (Newton, 1977). As the landfill ages, the amount of moisture necessary to support further stabilization generally is reduced to a level necessary only to maintain residual microbial activity and may be reduced to about 30 percent (Pohland, 1975).

Parametric Considerations

Temperature--

Processes dependent on microbiological activity are influenced by temperature and, because the majority of landfill stabilization tends to occur in the absence of free oxygen, anaerobic decomposition is of most significance. Anaerobic decomposition of refuse is similar to anaerobic sludge digestion processes which are often catagorized as mesophilic (20^{o}-$40^{o}C$) or thermophilic (50^{o}-$70^{o}C$). The usual trend is toward increased rates of anaerobic refuse decomposition and gas production with temperatures approaching $55^{o}C$; rates have been shown to decline sharply above this temperature (Farquar and Rovers, 1973).

During the early periods of landfill operations, oxygen (toxic to methane formers) is introduced with the refuse and is available for aerobic bioconversion until depleted. This oxidation process releases energy as heat which may cause an incipient rise in landfill temperature to a level capable of being sustained for some time because of the insulating nature of the landfill mass and the surrounding environment. This rise in temperature to as high as $70^{o}C$ also accelerates other important physical-chemical reactions associated with the overall progress of stabilization. However, landfill temperatures will normally fluctuate in accordance with ambient conditions (Pohland, 1975); these conditions will be site specific and influenced by the environmental setting for the circumstances under consideration.

pH and Associated Leachate Parameters--

As with the influence of temperature, anaerobic decomposition of refuse is influenced by pH, with an optimum range of 6.4 to 7.2 (Clark and Speece, 1970; Kotze, et al., 1969). Moreover, since refuse stablization and associated methane generation are pH dependent, it is important to consider the buffer conditions available and conveniently measured within the leachate phase. For instance, in a biochemically reduced environment similar to that encountered in most landfills (low ORP), certain oxidized species will be transformed to their reduced counterparts. Hence, nitrates and sulfates will be reduced to ammonia and hydrogen sulfide, respectively. Both of these species ionize in the leachate medium (the former as a weak base and the latter as a weak acid) and collectively influence its buffer intensity, pH and alkalinity. Concomitant changes to adversely high or low pH conditions would inhibit methane fermentation and further result in accumulations of volatile acids, frequent constituents in landfill leachates.

The pH established during a particular phase of landfill stabilization depends mainly on the relationship between the leachate volatile acids and alkalinity and the gas phase carbon dioxide content as originally described for anaerobic digestion processes by Pohland and Bloodgood (1963) and as further extended by Pohland and Suidan (1978). This has led to a recognition of a need for buffer capacity (expressed as alkalinity) greater than the volatile acids concentrations and some authors (Dague, 1968) have suggested augmentation with chemicals such as lime, sodium bicarbonate, caustic soda and ammonia. A similar procedure has been explored to augment accelerated anaerobic decomposition in landfills (Pohland, 1975; Leckie, et al., 1979).

Because of the many factors capable of influencing leachate pH at a given landfill site, it is not surprising that leachates from various landfill situations will vary dramatically not only in terms of pH, but also in terms of the other characterizing parameters discussed herein and illustrated in Table 2 (Pohland and Engelbrecht, 1976; Pohland, et al., 1983). Most of these parameters are linked to the nature of the wastes originally deposited and the degree or phase of stabilization or attenuation often loosely referred to as the "age" of the site.

As indicated in Table 2, landfill leachate can contain high or low concentrations of organic and inorganic constituents. The high concentrations of BOD_5, TOC, COD and total volatile acids characteristic of the former constituents are usually associated with a "young" landfill where leaching has only recently commenced and pH will be depressed into the acidic range as volatile acids accumulate and displace the normal bicarbonate buffer system. The relatively low pH will also influence the mobility of metals, although their concentration in the leachate will be also moderated by the opportunity for possible sorption, complexation, precipitation, ion exchange and/or oxidation-reduction reactions. Moreover, this potential is dependent on the nature and structural characteristics of the waste/soil mass, the actual availability of reactive species, and the acid-base (pH and alkalinity) and oxidation-reduction (ORP) conditions established within the leachate medium.

Because of the importance of anaerobic microbial conversion of waste organic constituents within a landfill, the sequence of events leading to refuse and leachate stabilization can be described as a staged process with acid production and methane fermentation constituting the most important phases (Pohland, 1980). The existence and duration of these phases are reflected in the various indicator parameters, i.e.: leachate pH and ORP are parameters indicative of acid-base and oxidation-reduction conditions, respectively, and critical to the proper assessment of acid formation and methane fermentation phases as indicated previously; TOC, COD, BOD_5 and total volatile acids (TVA) are indices of organic strength and relative biodegradability and are often used in ratio to each other to describe the degree of stabilization and/or "age" of the landfill (Table 3); and, nitrogen, sulfur and phosphorus and their oxidation states indicate nutrient sufficiency and also their availability for reaction and the condition (aerobic, anaerobic) of a particular phase of stablilzation. As indicated previously, similar importance can be ascribed to other parameters which may reflect such factors as buffer capacity (alkalinity), potential inhibition (heavy metals), ionic strength/activity (conductivity), migration potential (chlorides), and health hazards (coliforms, viruses and priority pollutants).

As indicated in Tables 2 and 3, ranges of concentration or intensity for leachate indicator parameters will vary throughout the life of a landfill depending not only on the reactions occurring at any one time, but also on the

TABLE 2. VARIABILITY OF LEACHATES PRODUCED DURING LANDFILL DISPOSAL OF MUNICIPAL REFUSE*

Constituent	Range of Concentration or Intensity
Chemical Oxygen Demand (COD), mg/L	31 - 89,520
Biochemical Oxygen Demand (BOD_5), mg/L	4 - 57,700
Total Organic Carbon (TOC), mg/L	70 - 28,000
Total Volatile Acids (TVA), mg/L CH_3COOH	0 - 18,800
pH	3.7 - 8.8
Oxidation-Reduction Potential (ORP), mV E_c	-240 - +163
Total Solids, mg/L	0 - 59,200
Total Dissolved Solids, mg/L	584 - 44,900
Total Suspended Solids, mg/L	10 - 700
Specific Conductance, μmoh/cm	1,400 - 17,100
Total Alkalinity, mg/L as $CaCO_3$	0 - 20,850
Total Hardness, mg/L as $CaCO_3$	0 - 22,800
Total Phosphorus, mg/L as P	0 - 130
Orthophosphorus, mg/L as P	6.5 - 85
Ammonia Nitrogen, mg/L as N	0 - 1,106
Nitrate + Nitrite Nitrogen, mg/L as N	0.2 - 51
Sulfate, mg/L	1 - 1,558
Sulfide, mg/L	0.9 - 818
Calcium, mg/L	50 - 7,200
Chloride, mg/L	4.7 - 5,000
Sodium, mg/L	0 - 7,700
Potassium, mg/L	28 - 3,770
Manganese, mg/L	0.09 - 125
Magnesium, mg/L	17 - 15,600
Iron, mg/L	0 - 2,820
Zinc, mg/L	0 - 370
Copper, mg/L	0 - 9.9
Cadmium, mg/L	0.005 - 17
Lead, mg/L	0.10 - 2
Chromium, mg/L	0.02 - 18
Nickel, mg/L	0.02 - 79

*Adapted from Pohland and Engelbrecht, 1976 and Pohland, et al., 1983.

TABLE 3. RELATIONSHIP BETWEEN LANDFILL AGE, LEACHATE COD AND RATIOS OF LEACHATE COD/TOC AND BOD_5/COD*

Landfill Age	Leachate Characteristics		
	COD, mg/L	COD/TOC	BOD_5/COD
Young (<5 years)	>10,000	>2.8	>0.5
Medium (5-10 years)	500 - 10,000	2.0 - 2.8	0.1 - 0.5
Old (>10 years)	<500	<2.0	<0.1

*Adapted from Chian and Dewalle, 1977

effects of washout and apparent dilution consequenced by continuous leaching. This latter effect will tend to diminish concentrations with time, but will not influence the total mass of leached constituents. Unfortunately, dilution effects are often not recorded, leading to analytical variances in both magnitude and interpretation when analyses are based upon concentration alone.

Gas Production and Quality--

The stabilization events occurring as landfills age will inevitably result in a period during which gas is released from microbiological degradation of organics associated with the deposited wastes. The magnitude and character of this gas production are affected by many variables including the nature of the waste and environmental conditions as introduced previously. These factors have been reviewed in detail by Rees (1980), Pohland, et al. (1983) and Halvadakis, et al. (1983). Of particular significance are sufficiency of biodegradable substrate including nutrients (N and P), favorable environmental conditions (moisture content, pH, temperature, buffer capacity and absence of inhibitors), and the potential for formation of localized "micro-environments" which may be isolated from the conditions prevailing in the bulk of the waste mass.

Because of the variability in the factors influencing gas yield at landfill sites, a production rate from a unit of refuse mass is yet a matter of conjecture. Various techniques have been developed to predict gas yields including stoichiometric methods (Anderson and Callinan, 1970; Alpern, 1973; Boyle, 1976) based upon a representative chemical formulation for municipal solid wastes, and weighted biodegradability methods (Golueke, 1970; Pfeffer, 1974; Dair and Schwegler, 1974; EMCON, 1980) based upon an assumption of biodegradability. From these theoretical techniques, total and methane gas yields range between 0.12-0.46 m^3/kg dry waste and 0.06-0.25 m^3/kg dry waste, respectively. Unfortunately, such predictions fail adequately to account for those previously identified factors which may limit microbially mediated gas generation and reduce the gas yields in an actual landfill setting. Such an eventuality is dramatically illustrated by the data presented in Table 4 where actual total and methane gas yields from a variety of reactor, lysimeter and field studies on refuse decomposition under anaerobic conditions ranged from 0.001-0.25 m^3/kg and 0.001-0.07 m^3/kg, respectively.

TABLE 4. GAS YIELDS FROM EXPERIMENTAL STUDIES ON ANAEROBIC BIOLOGICAL TREATMENT OF MUNICIPAL SOLID WASTE

Reference	Gas Yield, m^3/kg (STP)	
	Total	CH_4
Merz and Stone, 1964	0.013	--
Merz and Stone, 1968	0.004	--
Ramaswami, 1970	0.001-0.18	0.001-0.07
Rovers and Farquar, 1973	0.006	0.001
Augenstein, et al., 1976	0.25	0.13
DeWalle, et al., 1978	0.001-0.018	--
Walsh and Kinman, 1979	0.003-0.018	--
Pohland, 1980	0.007	0.004
Buivid, 1980	0.001-0.23	0.001-0.14
Chang, 1982	0.007-0.022	0.004-0.016

Landfill derived gases typically consist of 40-60 percent methane with the remainder consisting primarily of carbon dioxide (Table 4) and traces of other gases (N_2, O_2, H_2S) and organic vapors (organic acids and mercaptans) as recorded by EMCON (1977 and 1980), Lofy (1981) and ESCOR (1982). The degree of variation in gas quality is again dependent upon the nature of the microbially mediated processes established at the time of analysis and may vary considerably if these processes are being curtailed particularly by the presence of inhibitors. Therefore, gas production and quality can be used as additional evidence of the condition and phase of stabilization as a landfill matures.

CODISPOSAL

Codisposal with municipal refuse at landfills was traditional for many types of commercial and industrial wastes and continues to be practiced particularly in situations where small quantities or household contributions are excluded from regulatory monitoring or control. Many industrial wastes reach landfill disposal sites in the form of sludges which are then characteristically mixed with the municipal refuse. Studies on such codisposal practices have been reported (Bromley and Wilson, 1981; Jones, 1982) with an indication that certain quantities can be received at a municipal landfill site without deleterious effects on the stabilization process or the environment.

Newton (1977) conducted pilot-scale studies on the leaching of industrial wastes in simulated landfills and concluded that the presence of industrial wastes (oil/water emulsion, metal hydroxide sludge, and cyanide waste), with the exception of the cyanide waste, did not affect the composition of municipal solid waste leachate. Other research reported by Streng (1976, 1977), Swartzbaugh, et al., (1978) and Walsh and Kinman (1979, 1980 and 1981) on a total of 19 simulated landfills, constructed to study different mixtures of municipal refuse, sewage sludge and industrial wastes (petroleum, battery brine, electroplating, inorganic pigment, chlorine production brine and solvent-based paint sludges) under the influence of various infiltration rates and pH buffering, generally indicated that the admixtures appeared to have little effect on organic, nutrient and biochemical parameters, at least insofar as the data were analyzed by the authors.

Of particular interest to the studies presented later in this report were the results obtained by these authors on the codisposal of electroplating sludge. When compared to the leachate of the control, higher pH, increased alkalinity, higher total solids, reduced TOC and variable release of metals were observed; Fe, Cu, Pb, Cd and Zn concentrations were lower, Cr and Hg were the same, and Ni was higher than the control. Moreover, the gas production results indicated a cyclic production of methane possibly suggesting intervals of inhibition or inadequate gas production measurements. Similar inhibition or loss of gas production tended to occur for all industrial waste codisposal circumstances in the early stages of the studies, but when combined with other data over the 10-year experimental period, washout was suggested as the most dominant mechanism of reduction in leachate constituents. Therefore, these data are currently being re-evaluated in a retrospective analysis.

Myers, et al. (1980) reported on simulation studies of codisposal of municipal solid wastes with untreated industrial wastes and with chemically stabilized wastes (electroplating, chlorine production brine, and calcium fluoride/sewage sludges) in large landfill lysimeters. Results of analyses on the leachate generated during nine months of leachate production, when compared to a control cell, indicated that chemical stabilization significantly reduced the leaching of toxic metals. Either treated or untreated electroplating wastes had little effect on leachate quality; the calcium fluoride/sewage sludge tended to improve leachate quality.

Collectively, these results indicate that uncertainty prevails regarding the efficacy of codisposal of industrial wastes with municipal refuse in landfill sites. The results reported in the literature to date have not established acceptable quantities of such wastes, the effects of such wastes on the process of stabilization, and the operational control strategies that should be employed under such codisposal circumstances. The final results of the research presented herein should provide some insights into these issues; preliminary results reported previously by Pohland, et al., (1980, 1981 and 1982) will be employed to augment this report.

SECTION 4

MATERIALS AND METHODS

EXPERIMENTAL FACILITY

Four simulated landfill lysimeter columns, three test and one column, were constructed on the campus of the Georgia Institute of Technology. These four lysimeter columns were used in previous leachate recycle studies (Pohland, 1975) and were refurbished to be operationally similar to the units indicated in Figure 1. The units were constructed 4.27 m high by joining sections of 92-cm diameter ARMCO corrugated steel pipe with an effective volume of about 1800 liters. The pipe sections were lined with two coats of epoxy paint and placed on a wooden support structure secured with steel angles bolted around the base of each column. A conical concrete bottom with a 3.8-cm drain was formed in each simulated landfill to seal the bottom of the pipe section and facilitate drainage and collection of leachate. A 23-cm layer of coarse gravel (1.90-5.0 cm diam.) was placed in the bottom of each column to prevent clogging by the compacted wastes eventually added to each column.

After the units had been constructed, all sample points and connections were caulked with a sealing compound to prevent leakage. Leachate collection from the lysimeters was provided by epoxy-lined, 208-liter drums. A 3.81-cm ABS plastic pipe was used for leachate drainage from the conical base of each simulated landfill into collection sump. Two equipment sheds were assembled to house the leachate collection sumps, the centrifugal sump pumps used to recycle leachate, and the other instrumentation as well as to provide insulation, security and exclude rainfall and outside contaminant. Leachate collected in the sumps was recycled by pumping to distribution arms buried between the top of the compacted wastes and the soil cover contained in each column.

Leachate flow was designed to percolate by gravity to the collection sump. Temperature probes were inserted in each lysimeter through openings in the sides and a sample port was provided for each lysimeter at the point where the drain pipe discharged to each sump. All columns were insulated prior to loading with the bulk municipal solid waste and metal plating sludge. Provisions were provided for tap water addition to allow the rapid attainment of indicated field capacity and to facilitate associated leachate recycle and sampling. Thereafter, since the columns were each open at the top, rainfall was allowed to penetrate the wastes as it occurred.

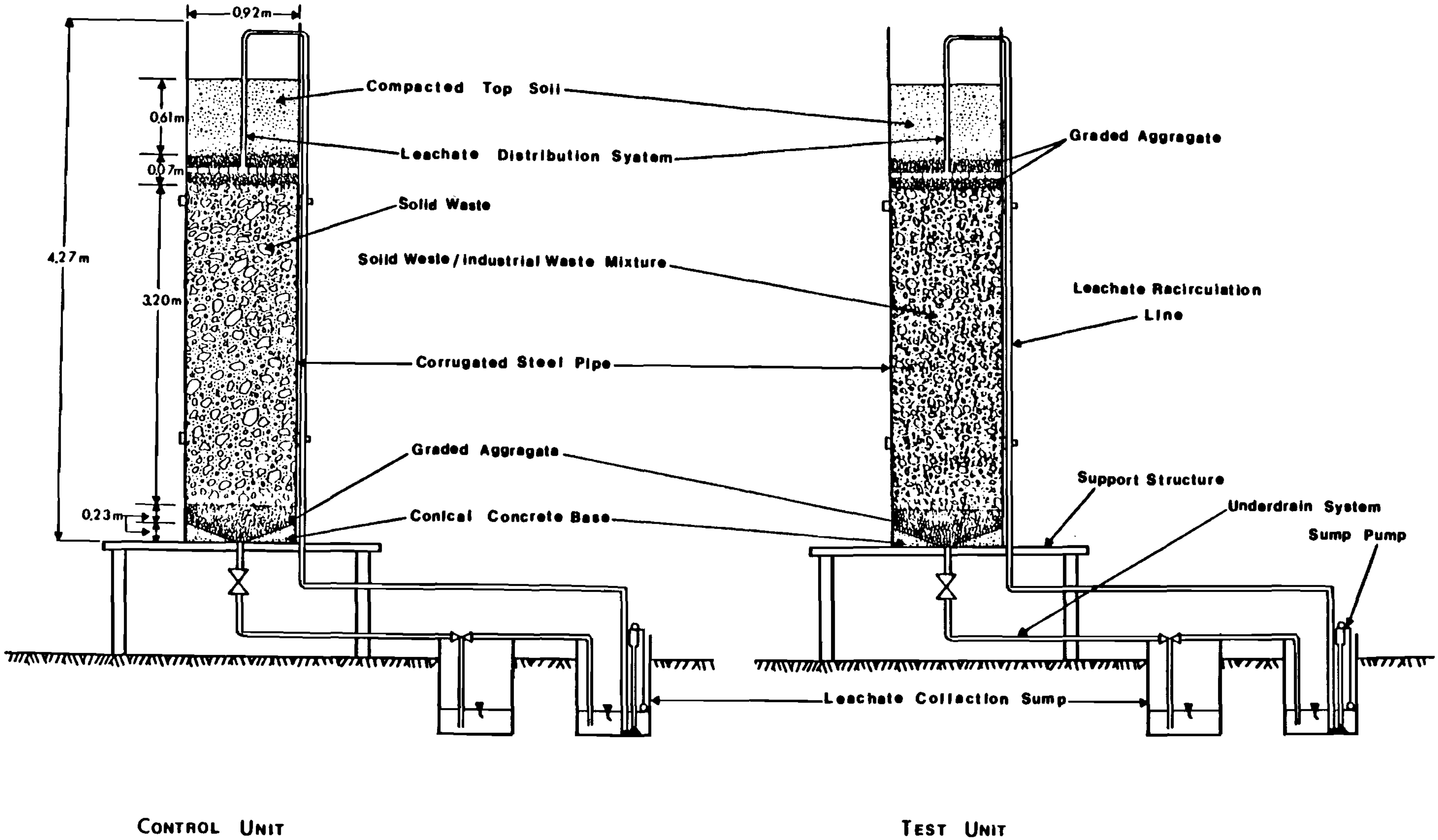


Figure 1. Simulated Landfill Columns with Leachate Collection and Recycle

WASTE CONSTITUENTS

After construction and instrumentation of the four simulated landfill columns were completed, waste acquisition and filling operations were initiated. The municipal refuse was collected from a residential area in Dekalb County, GA and delivered in bulk by a 23-m^3 compactor vehicle. Separation into categories and analysis of about 25 percent of the refuse yielded the characteristics presented in Table 5.

The metal plating sludge was obtained from a local metal finishing operation; Dixie Industrial Finishing Co., Inc. of Tucker, GA. This plant employs zinc plating, chromating and, to a lesser extent, plating of cadmium and nickel. All of these metals are considered to be hazardous and toxic. An alkaline sludge is produced after treatment of the continuous flows from rinsing operations and batch dumps of cleansing solutions. All chromium-containing wastes are collected and treated with sodium bisulfite to reduce hexavalent chromium to the trivalent form at a pH of 2.0 to 2.5. The reduced chromium wastes are then combined with the other wastes and the pH is raised with 50 percent liquid caustic soda to approximately 10 while calcium chloride and a polymer are added. This treatment results in precipitation of trivalent chromium and the other metals as hydroxides. The polymer addition causes a floc to form which aids the settling of the mixed metal hydroxides in a lamella settler. The underflow from the lamella settler is pumped to the clarifier where it is further concentrated and then centrifuged to about 20 percent solids. Samples of this sludge were analyzed for total metals content and other parameters as indicated in Table 6. Sawdust (Table 5) was added to this sludge to transform it to a more manageable consistency and to simulate probable admix procedures used at an actual landfill site.

TABLE 6. CHARACTERISTICS OF METAL SLUDGE CODISPOSED WITH MUNICIPAL SOLID WASTES IN SIMULATED LANDFILL INVESTIGATIONS

Parameter	Analysis
Moisture Content, %	84.7
Volatile Soldis, % dry	24.6
Zinc, mg/kg dry	317,000
Chromium, mg/kg dry	21,000
Nickel, mg/kg dry	400
Cadmium, mg/kg dry	13,100
Copper, mg/kg dry	185
Iron, mg/kg dry	94,000

Note: Total metals as determined after acid digestion (Appendix Table-A1).

TABLE 5. CHARACTERISTICS OF BULK MUNICIPAL SOLID WASTES AND SAWDUST USED IN SIMULATED LANDFILL CODISPOSAL INVESTIGATIONS

Waste Category	Wet Wt., %	Moisture, %	Volatile Solids, %	C, %	H, %	N, %	Heating Value, kJ/kg dry
Paper	53.0	11.6	87.5	41.57	6.76	0.07	15,114
Glass	13.7	-	-	-	-	-	-
Plastic and Leather	8.4	2.5	98.6	82.88	8.89	0.06	37,932
Diapers	2.9	2.1	98.2	46.89	6.04	0.55	20,432
Garden Debris	1.8	0.7	92.4	45.03	5.90	0.09	16,873
Food Wastes	6.2	75.4	92.0	41.76	6.61	1.97	18,966
Wood	2.0	-	-	-	-	-	-
Metals	5.9	-	-	-	-	-	-
Fines	6.1	45.1	90.0	40.65	5.47	0.97	15,282
Sawdust*	-	7.6	88.1	43.41	5.94	0.09	17,961

*Separately added to metal plating sludge (Table 6).

One of the columns (Column 1) served as the control and received 400 kg of bulk residential refuse and sawdust without any metal sludge; the other three columns (Columns 2, 3 and 4) received the same amount of residential refusetogether with 33.6, 65.8 and 135.2 kg of bulk metal sludge, respectively. The refuse and/or metal sludge in each case was mixed with 37.3 kg of sawdust and placed in successive layers throughout the columns as the columns were being filled to a final waste depth of 3.20 m (Figure 1). Each column was then covered with 61 cm (454.5 kg) of soil above the waste mixture and gravel/preforated pipe distribution system.

The amount of sludge/sawdust mixture placed in each column was based upon preliminary investigations on handling, leaching and potential sorption-desorption characteristics. The amounts chosen for the test columns were selected to cover a range between no effect to definite effect on the landfill stabilization processes and/or leachate quality. Sawdust added to the control column was intended to duplicate its contribution to landfill behavior in the sludge-containing simulated landfills.

FACILITY OPERATION

Leachate production was initiated by addition of tap water to each column until leaching commenced. Varying quantities of tap water with rainfall were introduced at different times to allow the simulated landfill cells to attain indicated field capacity and provide sufficient leachate samples for analysis. A record of the amount of tap water and rainfall intercepted by the simulated landfill columns is presented elsewhere in this report (Table 12 and Figure 12). Each simulated landfill column received the same amount of tap water and rainfall.

Recycle of the available leachate was commenced on Day 28 and was continued in an attempt to normalize the concentration of leachate constituents extractable from each of the simulated landfill columns. Except for instances when no leachate was available for recycle, or unless otherwise noted, leachate recycle was conducted at a frequency of one liquid volume recycle per day. Actual pumping time required to recycle accumulated leachate was about five minutes; the time required for the leachate to flow through each column slowly increased from three to four hours for Column 4 to about eight hours for the other three columns by Day 387. The difference in flow time was anticipated as variations in column behavior were established in response to each column loading tactic.

Total accumulation of leachate in the columns by Day 290 was about 190 to 260 liters for Columns 1, 2 and 4; at this point, Column 3 had only accumulated 120 liters of leachate. About 900 liters of rainfall and tap water had been added to each of the columns by Day 290. By Day 374, the quantity of leachate available for recycle in the four experimental columns diminished to about 28, 0, 30 and 120 liters in Columns 1, 2, 3 and 4, respectively. This decrease in available leachate was consequenced by the removal of some quantity required for sampling (approximately 500 mL per column) and also by the fact that little moisture was added (only 68 liters between Days 290 and 374) during a time when very hot and dry conditions prevailed (July-September, 1980). The reduction in accumulated leachate could have been an indication that complete saturation of the total contents of the columns had not been attained or maintained at that time and/or that moisture was being lost through evaporation.

By Day 387, leachate generation also ceased for Columns 1 and 3, however, Column 4 continued to generate about 100 liters of leachate which was recycled daily as it accumulated or at most, twice per day. This procedure also caused a decrease in the quantity of leachate from Column 4 so that by Day 404, only 20 liters of leachate remained. To accumulate sufficient leachate quantity to again initiate leachate recycle after the 1980 drought period, additional tap water was added to each column as presented and discussed in more detail later (Table 12 and Figure 12).

ANALYTICAL METHODS

Leachate samples collected from the control and three test columns were analyzed for 41 components as listed in Table 7. In addition to these, an attempt was made to analyze for sulfate concentrations. However, these efforts were stymied by matrix interferences as also encountered by others (Chian and DeWalle, 1977). No gas samples were collected, since the top of each column was open to the atmosphere.

Oxidation-reduction potential was measured with a Fisher Accumet pH Meter Model 144. The analyses for ammonia nitrogen, TKN, and orthophosphate were performed utilizing a Technican Auto Analyzer. All other analyses were performed according to Standard Methods for the Analysis of Water and Wastewater (1980). When specialized instrumentation was used, the specific instructions of the manufacturer were followed for operational details. The instrumentation utilized in analyses and the relative accuracy of analysis are listed with the respective analysis in Table 7.

Because of the central role of the volatile acids during landfill stabilization, five volatile acids (acetic, propionic, isobutyric, butyric and valeric) were determined by direct gas chromatographic techniques using a Perkin-Elmer Sigma 1 Gas Chromatographic System equipped with a Flame Ionization Detector. Separation was achieved using a 2 mm ID glass column,2 m in length, packed with 3% Carbowax m 20, 0.5% H_3PO_4 on 60/80 mesh Carbopack B. All samples were acidified with phosphoric acid and filtered through Gelman glass fiber filters (0.45 effective pore size) before analysis.

The precision and accuracy of this method and the long-term stability of the volatile acid samples and standards were assessed by the following three series of adjunct studies:

Series 1: The reproducibility of detector response, sampling and injection techniques, and the linearity of the analysis with respect to sample concentration and detector responses were examined by preparing five samples containing different concentrations of the volatile acids. Each of the samples was injected four times into the gas chromatograph. The results are summarized in Table 8. Based on the linear correlation coefficients, the variance of the detector response was less than nine percent of the mean.

TABLE 7. LEACHATE COMPONENTS MONITORED AND METHODS OF ANALYSIS DURING SIMULATED LANDFILL CODISPOSAL INVESTIGATIONS

Component	Method	Analytical Accuracy
Instrumental Techniques		
pH	Fisher Accumet pH Meter Model 144	1 $\pm$ 0.05 units
Oxidation-Reduction Potential (ORP), mV	Fisher Accumet pH Meter Model 144	$\pm$ 5 mV
Conductivity, μmho/cm	YSI Conductivity Bridge Model 31	$\pm$ 50 μmho/cm
Volatile Acids: Acetic, Propionic, Butyric, Isobutyric, Valeric; mg/L	Perkin-Elmer Sigma 1 Gas Chromatographic System	$\pm$ 5%
Total (TVA); mg/L as acetic acid		
Total Carbon (TC), mg/L	Beckman Total Carbon Analyzer Model 915	$\pm$ 5%
Total Inorganic Carbon (TIC), mg/L	Beckman Total Carbon Analyzer Model 915	$\pm$ 5%
Total Organic Carbon (TOC), mg/L	Beckman Total Carbon Analyzer Model 915	$\pm$ 5%
Ammonia Nitrogen, mg/L as N	Technicon Auto Analyzer	$\pm$10%
Total Kjeldahl Nitrogen, mg/L as N	Technicon Auto Analyzer	$\pm$10%
Metals, mg/L Fe, Ni, Mn, Cr, Cd, Mg, Cu, Na, K, Ca, Zn	Perkin-Elmer Atomtc Absorption Spectrophotometer Model 303	$\pm$ 5%
Orthophosphate, mg/L as $PO_4^{\equiv}$	Technicon Auto Analyzer	$\pm$10%
Noninstrumental Techniques*		
Chemical Oxygen Demand (COD), mg/L		$\pm$ 5%
5-Day Biochemical Oxygen Demand (BOD_5), mg/L		$\pm$10%
Total Solids (TS), mg/L		$\pm$10%
Total Volatile Solids (TVS), mg/L		$\pm$15%
Suspended Solids (SS), mg/L		$\pm$10%
Volatile Suspended Solids (VSS), mg/L		$\pm$15%
Total Dissolved Solids (TDS), mg/L		$\pm$10%
Volatile Dissolved Solids (VDS), mg/L		$\pm$10%
Sulfide, mg/L as $S^{=}$		$\pm$10%
Chloride, mg/L		$\pm$ 5%
Total Alkalinity, mg/L as $CaCO_3$		$\pm$ 5%
Carbohydrates, mg/L as glucose	Phenol-Sulfuric Acid Method	$\pm$20%
Aromatic Hydroxyls, mg/L as tannic acid	Folin-Denis Method	$\pm$10%
Carboxylic Acids, mg/L as acetic acid	Ferric-Hydroxmate Method	$\pm$20%
Proteins, mg/L as glycine	Ninhydrin Method	$\pm$20%

*Standard Methods (1980) procedures followed unless otherwise indicated.

TABLE 8. REPRODUCIBILITY OF DETECTOR RESPONSE AND LINEARITY OF ANALYSIS/ VOLATILE FATTY ACIDS ANALYSIS (SERIES 1)

Volatile Acids Concentration, mg/L*	Detector Response				
	Acetic	Propionic	Iso-Butyric	Butyric	Valeric
1000(500)	224611	180737	225655	226023	225533
	232890	191230	238907	242432	233085
	218008	173611	21728	221670	211197
	242097	193142	238780	239653	230982
800(400)	184640	145893	180504	184014	173614
	177554	141447	176466	178785	168384
	198099	157630	194529	198543	190645
	184857	148845	185466	190523	177387
600(300)	127484	102606	128220	129988	121943
	137448	110958	138946	142626	133241
	113607	109641	137874	140758	130326
	139149	113180	140688	142224	133402
400(200)	90509	73035	88952	89913	89296
	92008	73918	94062	95668	88733
	94072	75940	95813	96363	90141
	89821	72186	91020	94242	86171
200(100)	48468	39163	51371	51589	46319
	43999	37138	48520	49389	44506
	47057	38552	51689	51010	45864
	47704	39266	52980	54075	46257
Linear Regression:					
Intercept, mg/L	-1258	811	3943	4261	-1003
Slope, L/mg	230	367	450	456	448
Correlation Coefficient	0.993	0.996	0.999	0.996	0.999

*Acetic acid; (other acids).

Series 2: The reproducibility of standard sample preparation was determined using five replicate solutions of the acids at each of the concentrations used in Series 1. Each sample was injected one time. The results are summarized in Table 9. The ratio of the standard deviation to the mean varied from 0.014 to 0.094. This was considered within the range of established response variation.

Series 3: Since the long-term stability of standards and samples was of concern with respect to both sample storage and scheduling of analyses, the feasibility of preserving samples for future analysis was investigated by preparing five samples of different concentration and freezing seven aliquots of each for future analysis. The concentration of the original sample was determined by analysis against an independent set of standards. A new set of standards was prepared each day. The data, summarized in Table 10, indicate that losses ranged from greater than 20 percent for acetic acid to less than 10 percent for butyric and isobutyric acids.

The data from Series 1 and 2 of this evaluation of the volatile acid analytical methodology are presented in Figures 2 through 6.

With regard to other special analyses significant to these investigations, the modification of the Folin-Denis Method (Folin and Denis, 1912) for aromatic hydroxyls as presented by Standard Methods (1980) was further modified for use in this study. The reaction involves oxidation of the phenolic hydroxyl group, reduction of phosphomolybdotungstic acid, and subsequent color formation by addition of alkali. Extensive testing of the procedure (Smit, et al., 1955; Folin and Ciocaltegu, 1927; Chian and DeWalle, 1977) has yielded several conclusions including:

1. The number of hydroxyl groups on the ring is less important to color intensity than the position;

2. The wavelength of maximum absorbance was relatively insensitive to the test compound, but absorbance at the maximum was sensitive to the test compound;

3. High degrees of accuracy and precision can be attained; and,

4. The major interference is generally contributed by ferrous iron (2 mg/L will give a color equivalent of 1 mg/L of tannic acid), but other reducing agents such as sulfide and nitrite will also interfere.

All of these conclusions were confirmed in this study by the procedure outlined in Appendix Table A-2.

The phenol-sulfuric acid technique presented by Goltermann (1978) was utilized for the detection of carbohydrates. The reaction involves the formation of an osazone by reaction of hydrazine with the aldehyde group in an

TABLE 9. REPRODUCIBILITY OF STANDARD SAMPLE PREPARATION/ VOLATILE FATTY ACIDS ANALYSIS (SERIES 2)

Volatile Acids Concentration, mg/L*	Detector Response			
	Acetic	Propionic	Isobutyric	Butyric
1000(500)	225804	186499	229401	229666
	221388	182636	286304	228461
	229933	191607	234901	230736
	224821	185641	229083	228638
	220403	182634	225642	221746
800(400)	188624	147899	183642	185744
	188423	152643	182936	181338
	181493	144637	179632	181349
	179602	140092	177426	178631
	185304	146592	180394	180651
600(300)	130021	110642	135892	139421
	121318	99615	126418	128314
	132914	112694	135418	138899
	126572	106377	129479	131567
	120938	100957	127021	130292
400(200)	92108	73644	96401	93782
	90374	71008	92535	90425
	95462	77637	97928	90425
	89331	70568	92310	89429
	89429	71306	90618	88321
200(100)	45877	38652	50940	51986
	44514	39012	48871	50048
	39697	32384	45314	44929
	41378	34297	47735	46582
	47319	40642	51218	53052
Linear Regression:				
Intercept, mg/L	-2310	-1733	-2306	2125
Slope, L/mg	227	371	471	448
Correlation Coefficient	0.996	0.997	0.984	0.998

*Acetic acid; (other acids).

TABLE 10. EFFECTS OF SAMPLE STORAGE ON CONCENTRATION MEASURED/
VOLATILE FATTY ACIDS ANALYSIS (SERIES 3)

Standard Sample	Storage Time, days								% Decrease	
	0	1	2	3	4	5	10	30	10d	30d
Acetic Acid										
1000 mg/L	1072	922	938	918	906	892	888	860	17.2	19.8
800 mg/L	794	705	712	692	701	686	652	651	17.9	18.0
600 mg/L	609	542	538	551	521	492	488	475	19.9	22.0
400 mg/L	427	362	365	358	342	331	340	326	20.4	23.7
200 mg/L	191	181	185	172	163	156	149	138	22.0	27.7
Propionic Acid										
500 mg/L	542	504	512	492	488	471	468	464	13.7	14.4
400 mg/L	426	391	386	378	371	375	362	365	15.0	14.3
300 mg/L	298	286	279	260	264	252	241	239	19.1	19.8
200 mg/L	207	194	189	182	185	179	171	172	17.4	16.9
100 mg/L	93	89	80	82	77	70	69	72	25.8	22.6
Isobutyric Acid										
500 mg/L	521	506	514	499	504	498	494	495	5.2	5.0
400 mg/L	406	402	397	400	391	386	387	382	4.7	5.9
300 mg/L	298	290	288	285	281	284	282	281	5.4	5.7
200 mg/L	204	198	200	191	190	186	191	189	6.4	7.4
100 mg/L	98	91	94	93	90	88	91	89	7.1	9.2
Butyric Acid										
500 mg/L	517	512	503	496	482	474	470	472	9.1	8.7
400 mg/L	398	381	387	379	375	375	372	374	6.5	6.0
300 mg/L	307	296	290	287	291	286	284	282	7.5	8.1
200 mg/L	198	191	189	190	186	185	181	183	8.6	7.6
100 mg/L	102	104	98	95	92	94	93	91	8.8	10.8

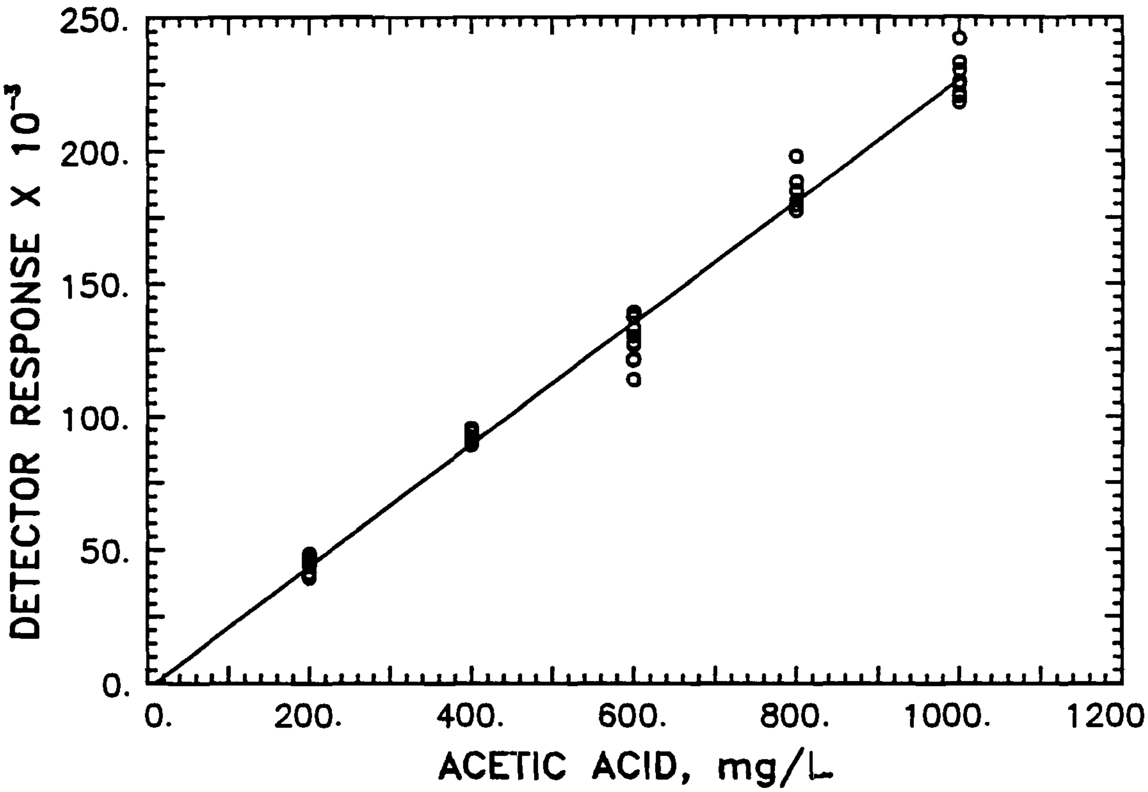


Figure 2. Acetic Acid Calibration Curve

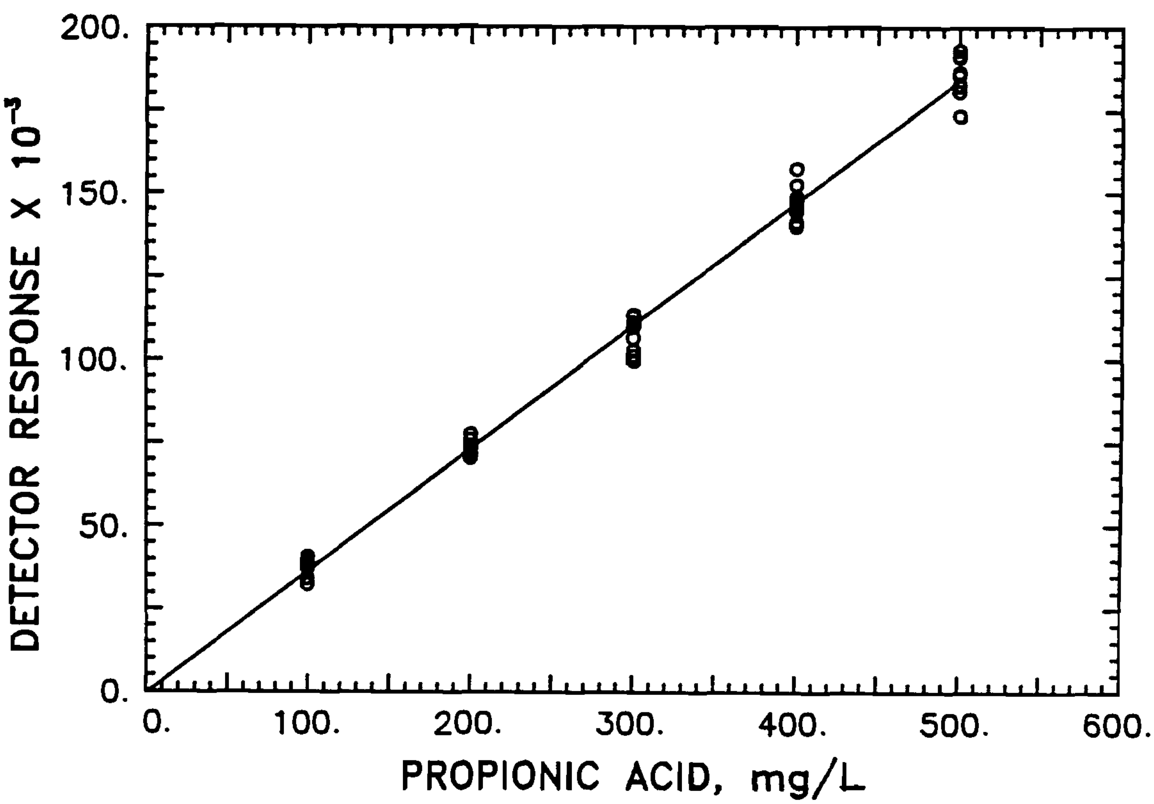


Figure 3. Propionic Acid Calibration Curve

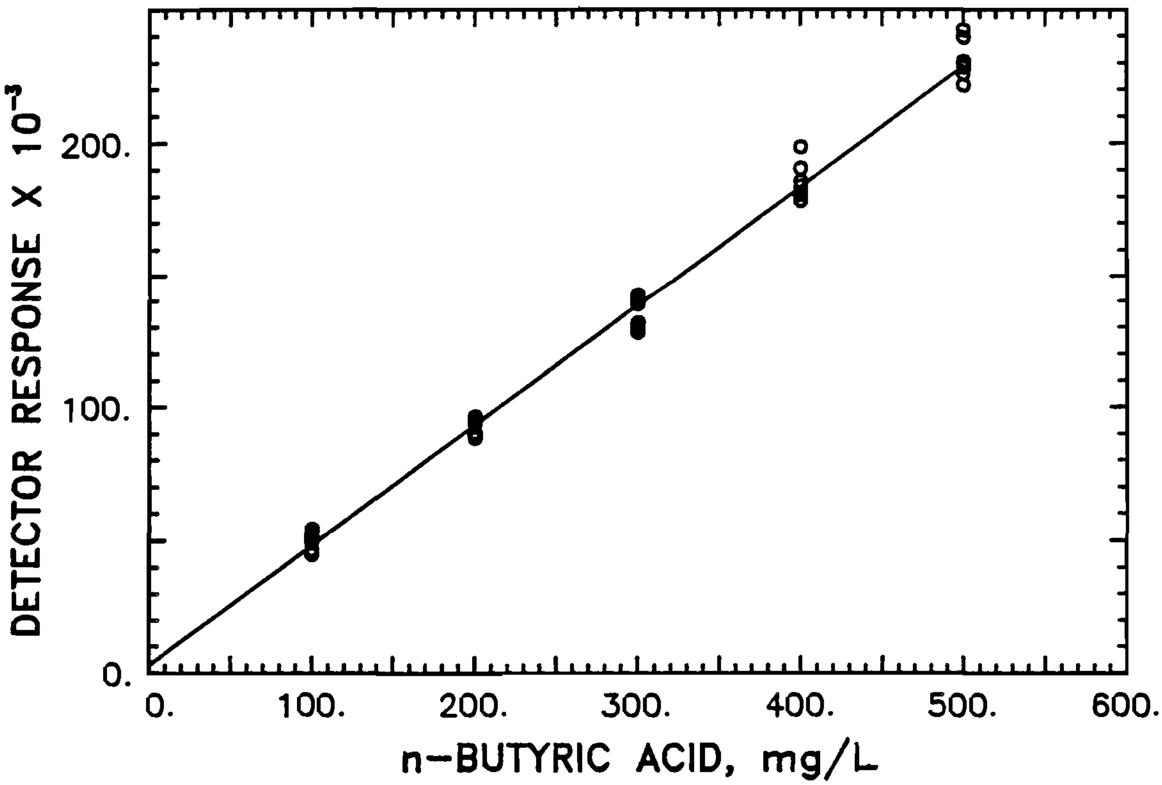


Figure 4. n-Butyric Acid Calibration Curve

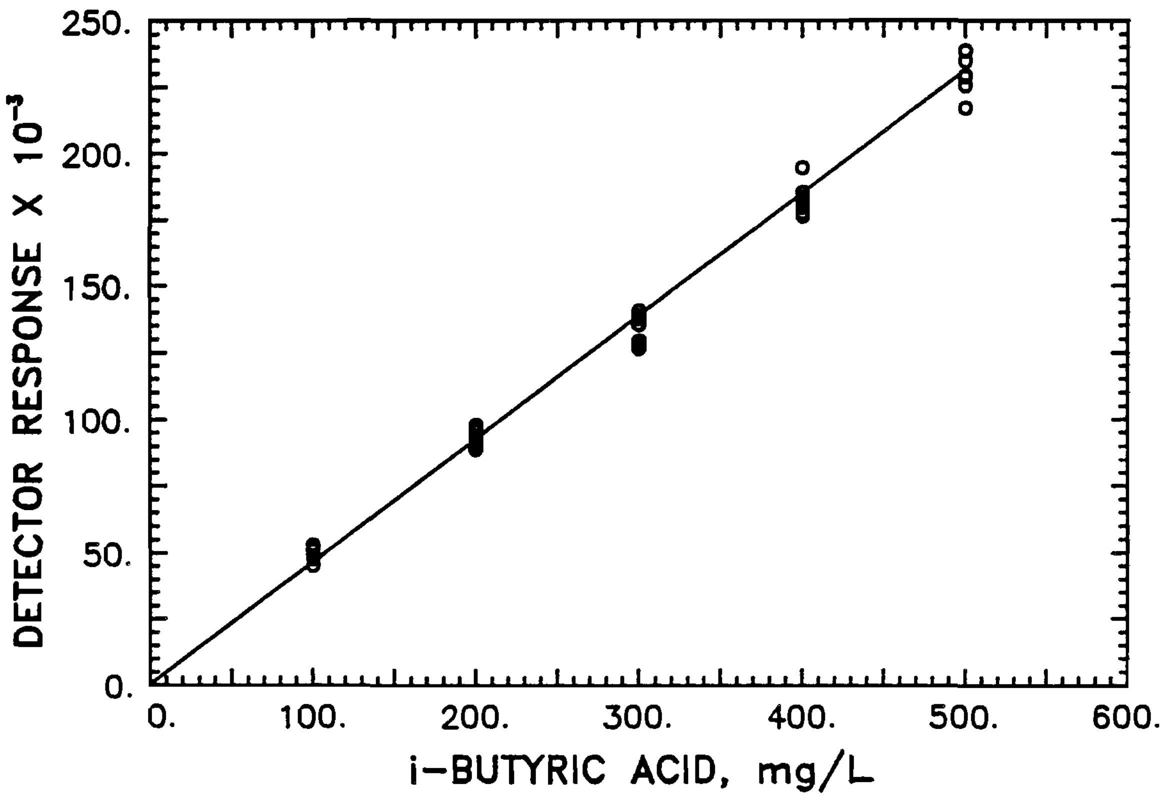


Figure 5. i-Butyric Acid Calibration Curve

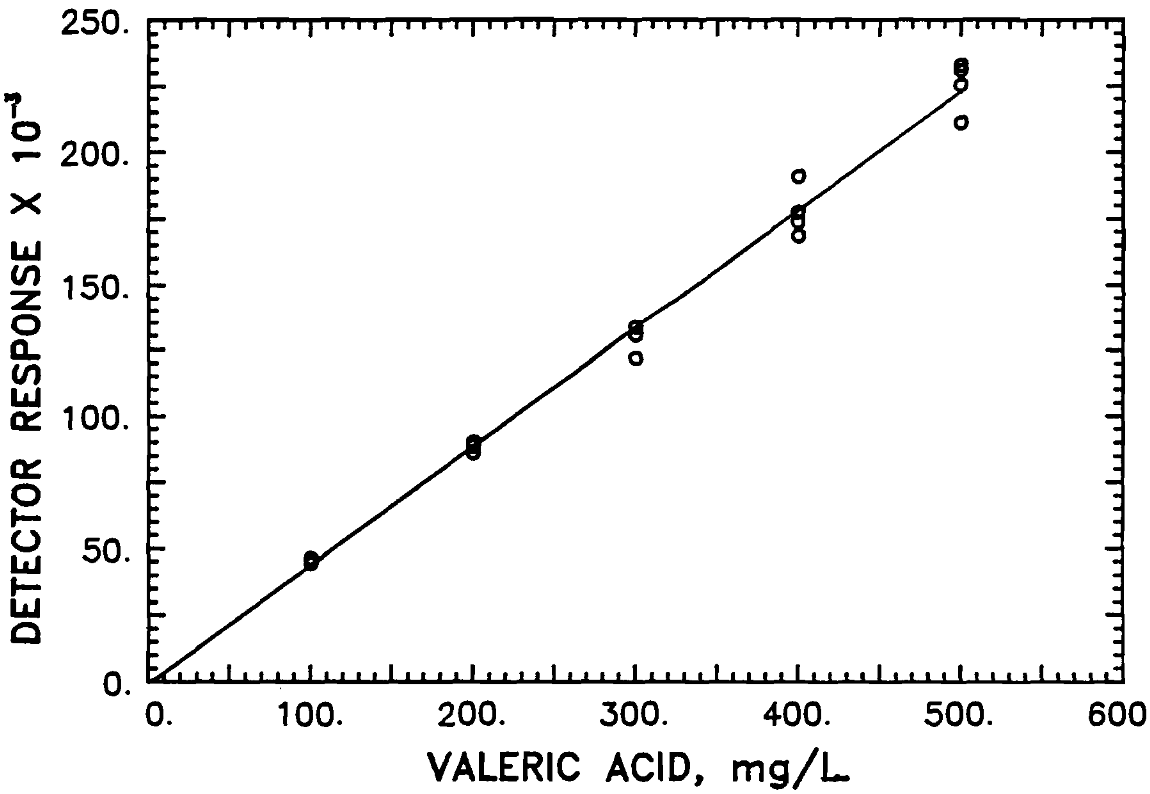


Figure 6. Valeric Acid Calibration Curve

acidic medium followed by reaction with phenol to form an azo dye. The colored product, using glucose as the reference compound, has an absorption maximum of 520 nm.

The hydroxylamine technique for carboxylic acids of Montgomery, et al. (1962), as modified by Chian and DeWalle (1977), was further modified for this study (Appendix Table A-3). The reaction involves the esterification of the carboxyl moiety by ethylene glycol in acidic media, formation of hydroxamate in alkaline media, and production of a colored ferric iron-hydroxamate complex in acidic media. The color formation was found to be rate dependent and as such, the modified procedure called for strict control of reaction times. Acetic acid was used as the reference compound, since it gave the highest absorbance at its wavelength of maximum absorbance and it was expected that, of the lower volatile acids, it would be the most abundant. Several straight-chain and branched-chain free volatile acids were examined. The wavelength of maximum absorbance for each compound was between 500 and 510 nm.

Proteins (amino acids) were analyzed by a modification of the method described by Snell and Snell (1937). In this method, the sample protein was hydrolyzed by heating 25 mL of leachate, to which had been added 1.0 mL of 10% HCl, in a boiling water bath for 30 minutes. The sample pH was then adjusted (~pH 5 to 9) with NaOH and 2.0 mL of 1.0% triketohydriclene hydrate (ninhydrin) were added. The blue color formed was measured spectrophotometrically at 650 nm. Reagent blanks were prepared by processing leachate samples similarly but without the addition of the ninhydrin. When necessary, samples and blanks were diluted to allow appropriate color development and analysis. The method was calibrated with glycine as a standard and all results were expressed in terms of mg/L glycine.

Metal concentrations for 11 metals were determined by atomic absorption spectrophotometry (Perkin Elmer Model 303). Prior to analysis, each sample was digested and concentrated by a factor of four according to the procedure given in Appendix Table A-4. Concentration of samples facilitated the detection of metals present at low concentrations.

SECTION 5

PRESENTATION AND DISCUSSION OF RESULTS

The research reported herein had as its primary goal, investigations of the behavior and fate of metal plating waste treatment sludges containing toxic heavy metals when codisposed with municipal solid waste in landfill where leachate management was being practiced. Therefore, the data obtained from these investigations were evaluated in two parts. In the first part, the impact of the toxic metals on the composition of the leachate and the implications of this impact with respect to landfill stabilization processes were examined. In the second part, factors within the landfill environment which impacted upon the mobility of heavy metals were considered. The time scale for data used throughout the presentation is in terms of time since initial loading of the simulated landfill columns (September 20, 1979) unless otherwise indicated.

ENVIRONMENTAL DATA

The weekly ranges in high and low ambient and internal column temperatures are reported in Table 11 and presented graphically in Figures 7 through 11 for about the first year of operation of the test facility. The internal temperature of each column and the ambient temperature were continuously monitored. An average weekly variation of 2°C-3°C occurred in the column temperature and only weekly ranges of temperatures are reported; daily temperature variations followed the same general trends.

The ambient temperature varied from 0°C to 40°C, with the high occurring in July 1980 and the low in February 1980. The column temperatures ranged from a low of 3°C to 4°C to a high of 32°C to 33°C. In all cases, the low temperatures occurred in February 1980 and the highs in July 1980. The variations in low and high temperatures were not so dramatic in the landfill columns due to some insulation that was placed around each landfill column on November 17, 1979 (Day 65 since loading). Significant differences between the landfill column temperatures were not observed. Although freezing conditions did not occur, temperatures were decreased sufficiently to help retard rapid biological degradation and/or removal of available organics from the leachates. However, since the variation in temperatures from column to column was not significant, this influence was not considered primarily responsible for the difference in landfill behavior observed in leachate analyses between the control and test units. Although not similarly recorded for the second year of the experimental studies, ambient temperature variations again followed the general seasonal trend observed during the first year.

TABLE 11. WEEKLY RANGES OF AMBIENT AND COLUMN TEMPERATURES DURING SIMULATED LANDFILL CODISPOSAL INVESTIGATIONS

Day	Ambient Temperature		Column Temperatures							
			Column 1		Column 2		Column 3		Column 4	
	Low, °C	High, °C	Low, °C	High, °C	Low, °C	High, °C	Low, °C	High, °C	Low, °C	High, °C
38	7	26	17	22	18	22	15	21	17	22
45	6	24	14	18	15	18	12	18	16	18
52	9	28	13	18	13	19	13	15	13	16
59	5	28	11	15	11	16	9	16	11	15
66	16	28	15	19	15	18	16	18	15	18
73	0	13	15	15	12	13	12	13	15	17
80	0	20	11	14	10	13	9	13	10	14
87	9	26	10	13	10	13	11	13	10	13
94	0	26	11	17	11	15	11	15	11	15
101	6	17	11	13	11	13	11	12	11	13
108	2	20	12	13	12	13	11	12	12	13
115	0	20	11	12	11	13	11	12	12	13
122	-	-	-	-	-	-	-	-	-	-
129	-	-	-	-	-	-	-	-	-	-
136	0	15	10	11	9	10	9	10	10	11
143	0	11	4	4	3	3	4	4	3	3
150	0	18	4	6	3	5	4	8	3	8
157	0	27	6	12	6	12	6	15	6	12
165	0	25	12	17	12	14	12	17	13	14
171	0	24	10	17	10	14	10	14	10	14
178	4	24	12	15	12	16	12	15	12	16
185	7	21	11	13	11	14	11	14	11	15
192	10	26	13	16	14	16	14	17	15	18
199	16	22	16	19	16	19	17	20	15	20
206	11	26	18	21	18	20	19	21	19	20
213	11	28	19	22	19	21	18	21	17	20
220	13	31	21	25	20	22	21	24	21	24
227	13	31	20	23	19	21	20	22	20	22
234	18	33	23	24	21	23	23	24	23	24
241	11	26	18	21	17	20	17	21	16	21
248	22	34	24	26	21	23	24	26	22	25
255	24	35	25	26	22	24	25	27	24	25
262	27	35	26	29	24	27	27	30	25	28

continued

Table 11. continued

Day	Ambient Temperature Low, °C	Ambient Temperature High, °C	Column 1 Low, °C	Column 1 High, °C	Column 2 Low, °C	Column 2 High, °C	Column 3 Low, °C	Column 3 High, °C	Column 4 Low, °C	Column 4 High, °C
269	28	38	26	27	24	26	26	27	25	
276	24	36	26	27	24	26	26	27	25	
283	24	35	27	29	26	28	27	29	27	
290	25	35	29	31	27	29	28	30	27	
297	28	40	30	32	28	31	29	32	28	
304	31	40	31	33	29	32	30	33	29	32
311	31	38	32	33	30	31	31	32	30	32
318	31	37	31	32	30	31	30	31	30	31
325	28	35	29	31	28	30	28	30	28	30
332	26	32	28	29	27	28	26	28	26	28
339	26	32	29	21	28	30	28	31	28	30

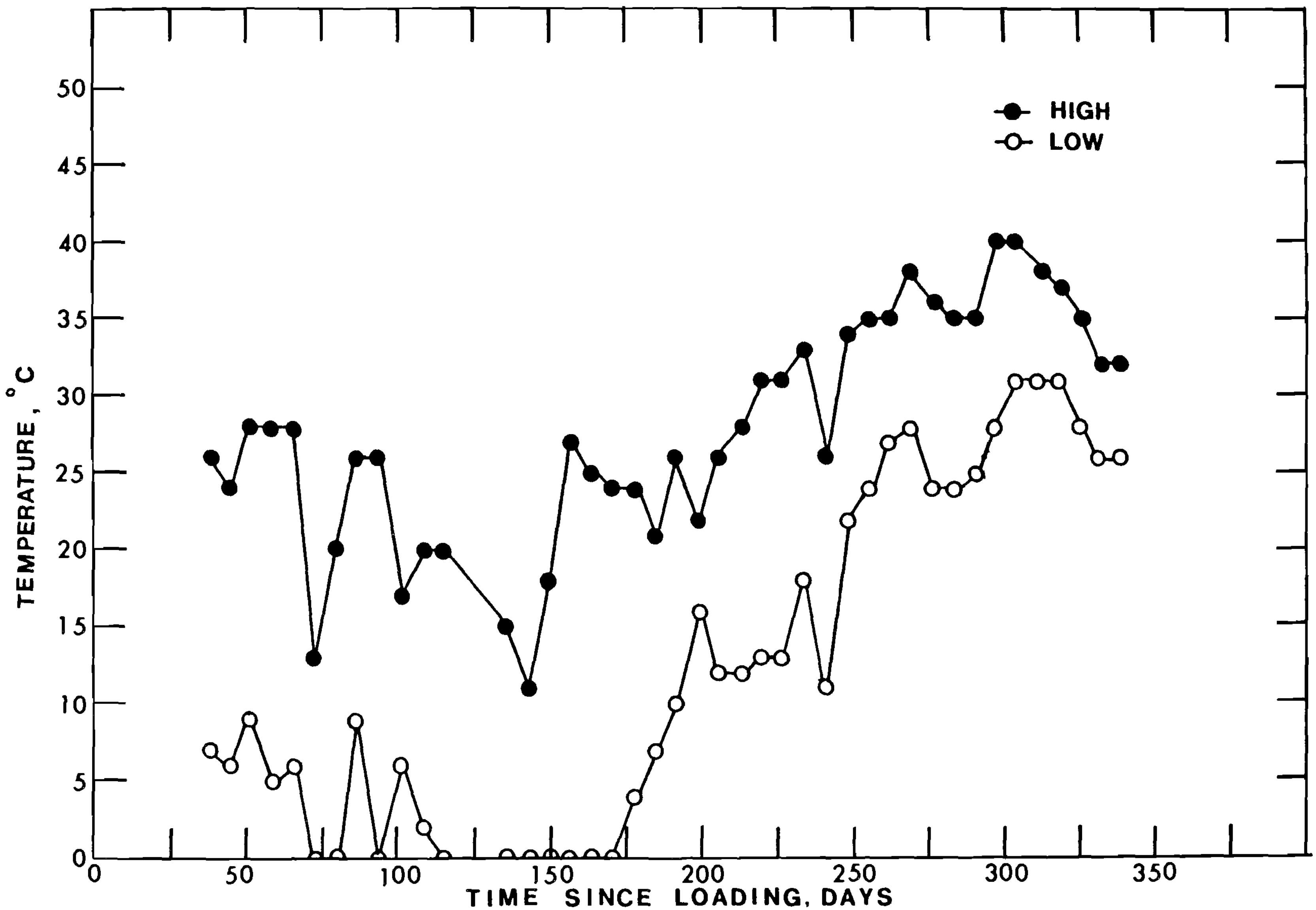


Figure 7. Weekly Ambient Temperature at Test Site

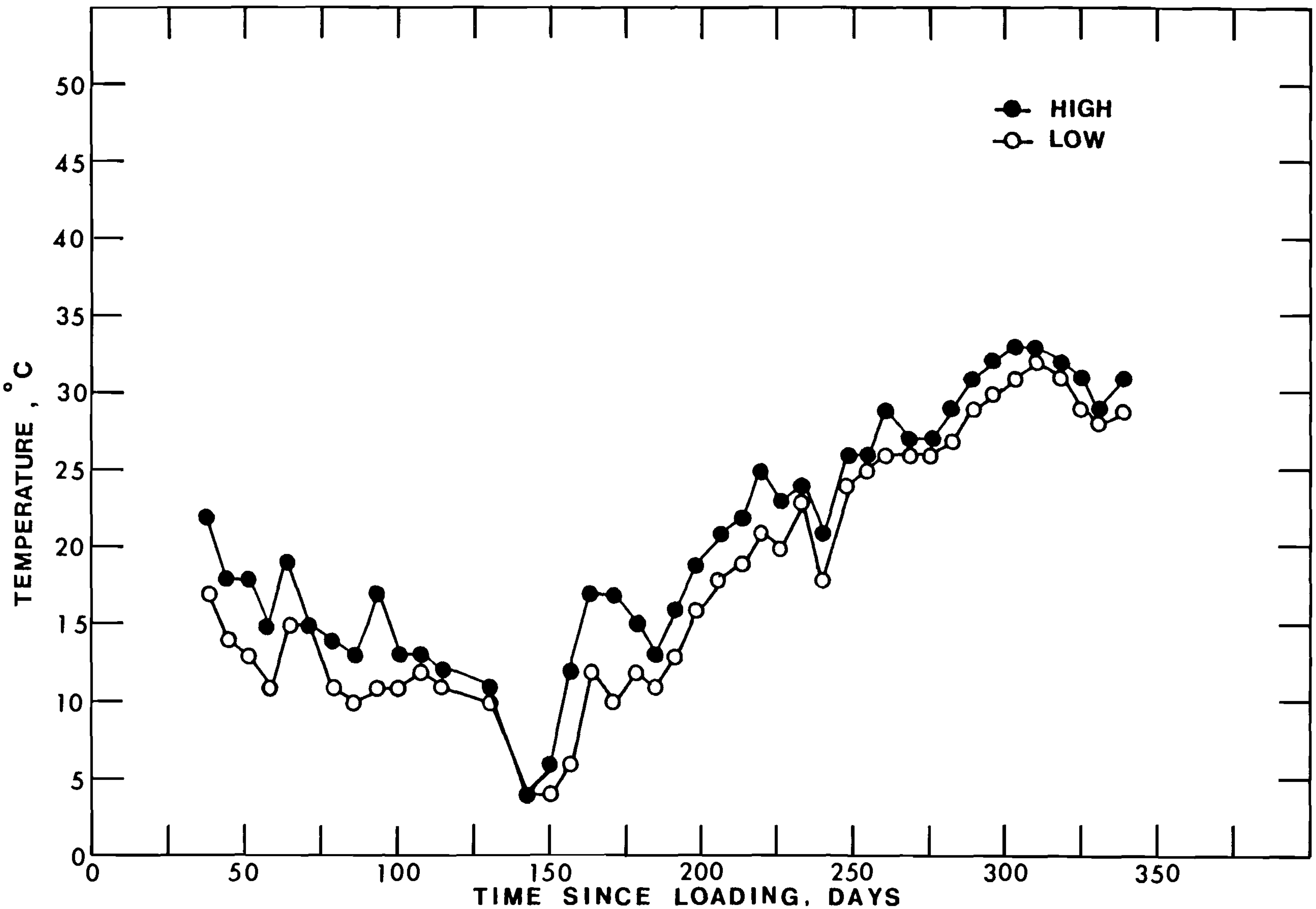


Figure 8. Weekly Internal Temperature of Simulated Landfill Column 1

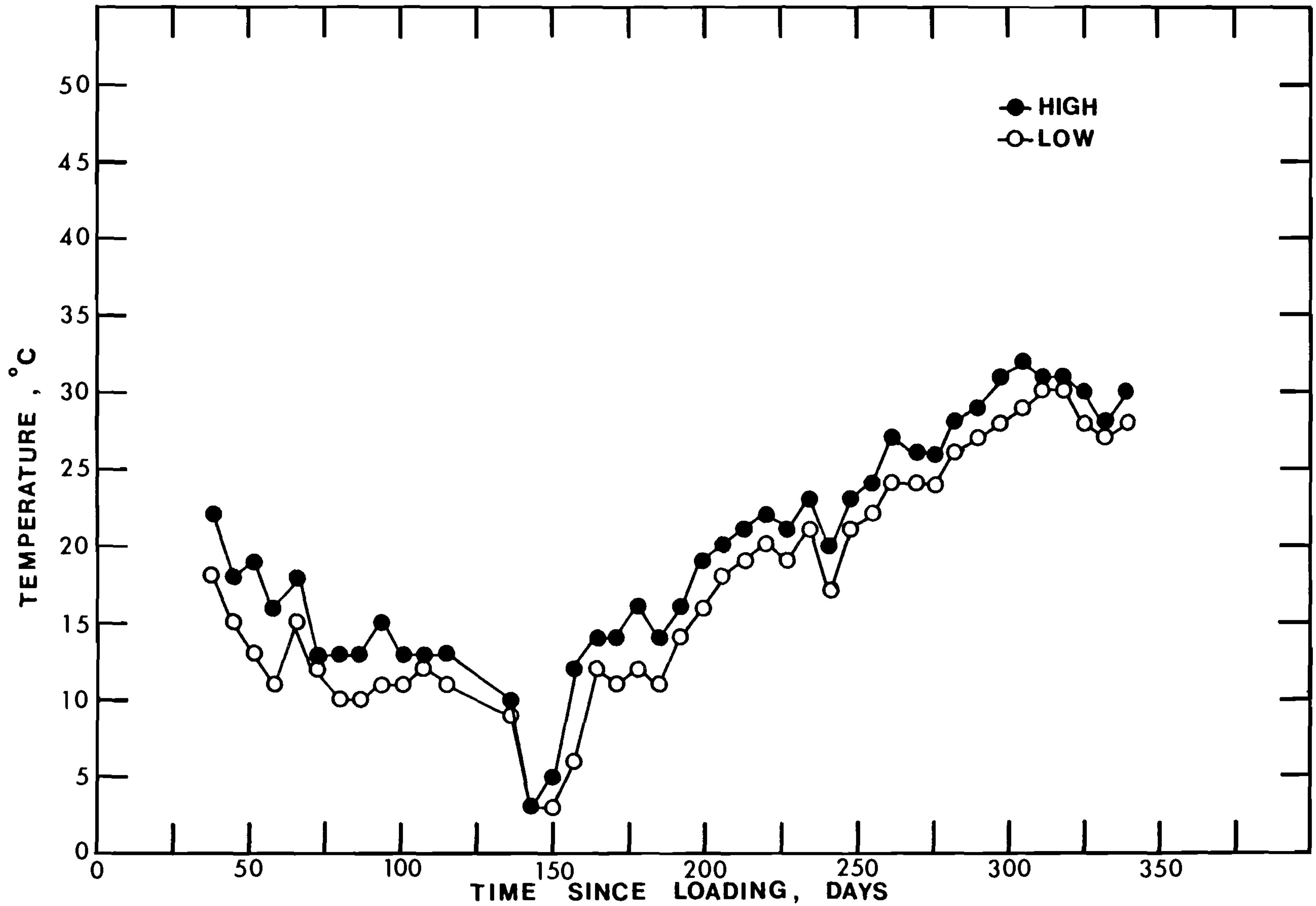


Figure 9. Weekly Internal Temperature of Simulated Landfill Column 2

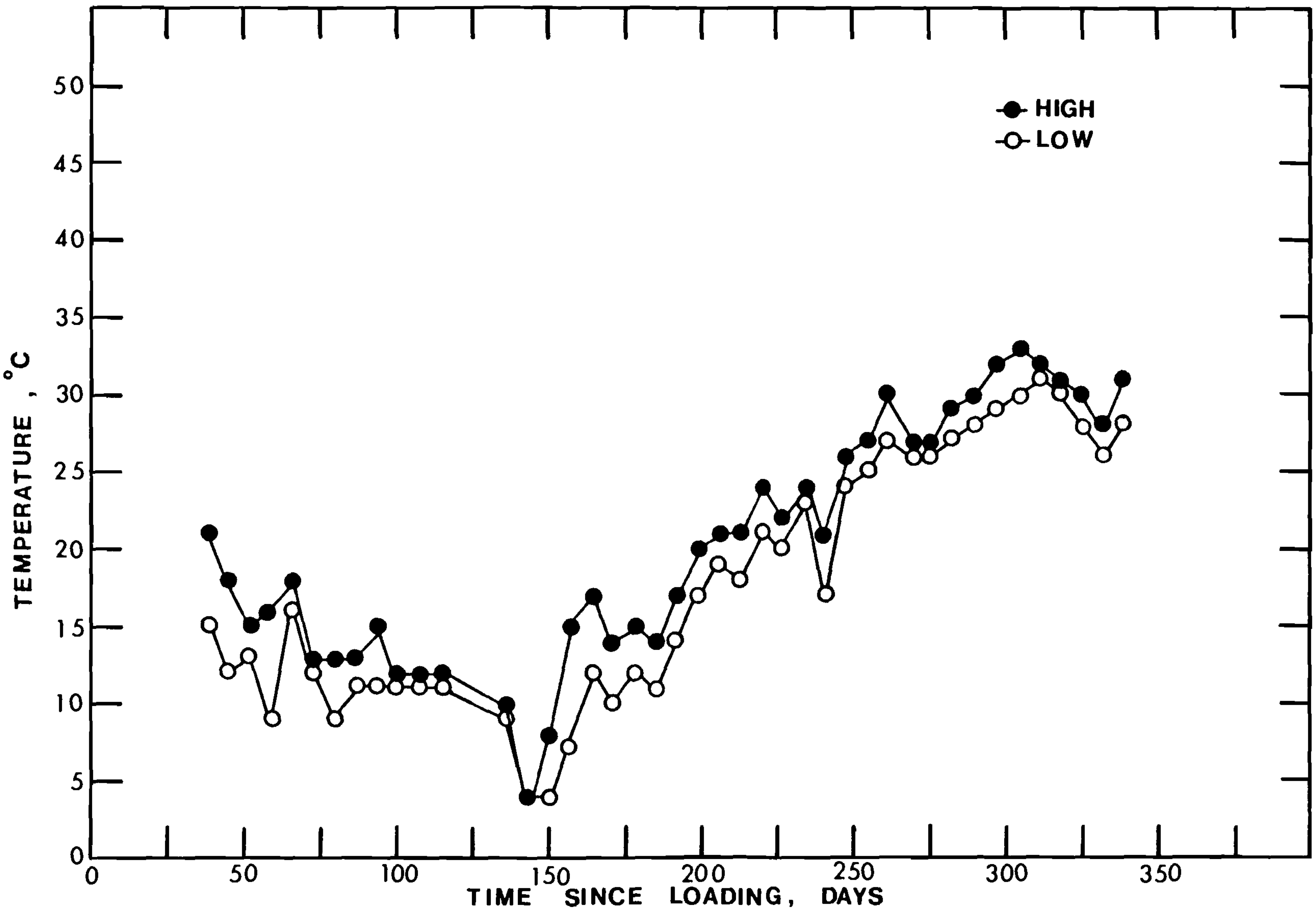


Figure 10. Weekly Internal Temperature of Simulated Landfill Column 3

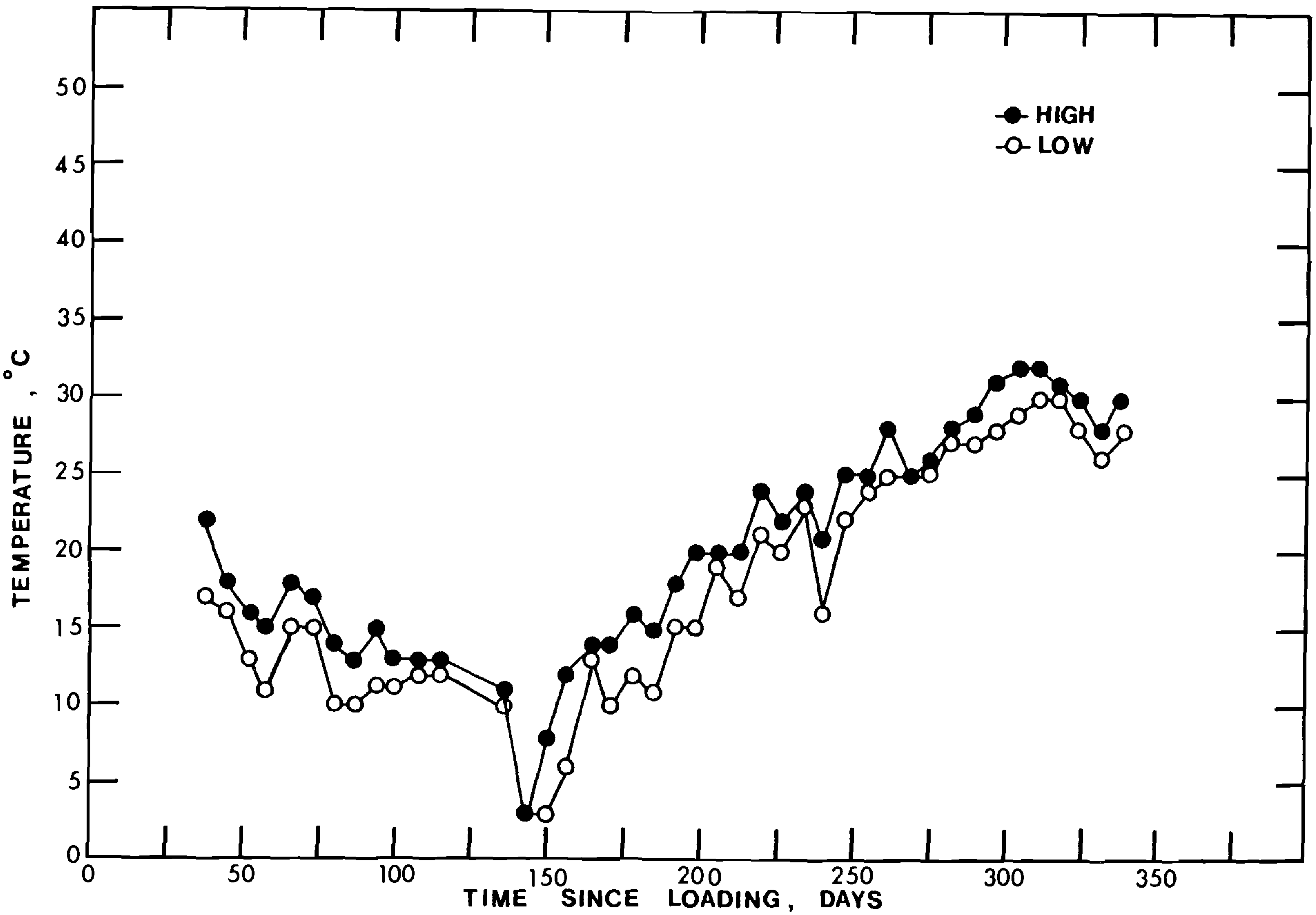


Figure 11. Weekly Internal Temperature of Simulated Landfill Column 4

The incremental and cumulative moisture and rainfall received by the simulated landfill columns are reported in Table 12. Figure 12 presents the cumulative moisture addition to each column since each landfill column intercepted the same amount of rainfall. Tap water was initially or later added in equal amounts to each landfill column to help establish indicated field capacity or to provide sufficient moisture to reinitiate recycle, respectively. (Each cm of moisture addition was equivalent to 6.65 liters of water.) As indicated here and in subsequent datapresentations, a period of drought commencing about Day 380 and lasting through Day 480 was encountered when no net leachate generation occurred. To simulate a period of landfill closure followed by possible loss in final cover integrity, no additional moisture (tap water) was added and new leachate was produced only after the drought condition had subsided and rainfall, augmented by tap water addition, led to its formation (Figure 12).

LEACHATE CHARACTERISTICS

Forty-one leachate parameters were monitored during the more than 700 days since loading of the columns was completed. The analytical data for the leachate samples collected during the experiments from Columns 1, 2, 3 and 4 are included in Tables 13, 14, 15 and 16, respectively.

Mass Computations for Indicator Parameters

As indicated in Tables 13 through 16, the initial data obtained for all parameters measured in these studies were developed in terms of concentration. While concentration provides an indication of the nature of the chemical environment within the landfills, it does not give an adequate measure of the total mass of a specific component present and/or removed in the leachate. Therefore, variations in mass not only reflect changes in chemical and biological activity, but also the impact of such physical factors as evaporation, dilution and sample withdrawal. For instance, a sudden decrease in metal concentration in the leachate may result not only from chemical precipitation, but from simple dilution due to rainfall or tap water additions. In such a case, efforts at drawing conclusions concerning the chemical behavior of the landfill based on concentration data alone would be exceedingly suspect and susceptible to error.

The estimation of solute mass requires a knowledge of both leachate concentration and total volume. Since the direct measurement of leachate volume contained in or released from the lysimeters being used in these studies was not possible, a technique based on the behavior of an abundant chemically and biologically conservative leachate component was used as an indicator of available leachate volume. Several parameters measured during this study met the requirements for such an indicator; i.e., presence in high concentrations at all times, measured with good analytical reliability, and not subject to significant precipitation, consumption or generation due to the associated processes of waste stabilization.

Of the three substances (sodium, potassium and chloride), which best fulfilled these latter requirements, chloride was selected as the parameter by which leachate volume could be estimated. Therefore, in computing the volumes

TABLE 12. MOISTURE OR PRECIPITATION ADDED TO THE SIMULATED LANDFILLS

Time Since Loading, days*	Moisture or Precipitation, cm***	Cumulative Moisture and Precipitation, liters
5	4.98	33.12
8	0.20	34.45
9	1.59	45.02
14	4.10	72.29
15	0.55	75.94
16	2.55	92.90
21	0.85	98.55
22	3.38	121.03
25	4.51**	151.03
26	13.53**	241.03
27	0.32	243.16
36	4.51	273.16
40	1.02	279.94
47	1.12	287.39
50	3.86	313.06
54	9.02**	373.06
58	2.78	391.55
59	1.27	399.99
72	2.87	419.09
73	0.75	424.06
84	2.59	441.29
108	0.58	445.14
114	0.18	446.34
119	1.62	457.11
122	1.30	465.76
124	0.42	468.55
128	8.05	522.09
139	1.02	528.87
152	8.10	582.73
158	3.64	606.94
164	2.70	624.89
180	6.60	668.78
197	8.80	727.30
208	1.57	737.75
226	4.75	769.33
247	0.89	775.25
254	17.20	889.63
282	2.21	904.33
324	8.20	958.86
373	1.45	968.50
387	12.20	1049.63
448	12.09**	1130.00
454	1.50	1140.00
483	0.29	1141.97
529	18.26	1263.41
539	2.59	1280.64
553	1.60	1291.29

continued

Table 12 - continued

Time Since Loading, days*	Moisture or Precipitation, cm***	Cumulative Moisture and Precipitation, liters
560	0.46	1297.34
571	8.59	1354.47
589	1.28	1362.98
596	0.54	1366.57
603	0.20	1367.90
610	4.21	1395.90
617	1.87	1408.34
624	4.02	1435.07
631	1.62	1445.84
641	6.63	1489.94
649	0.93	1496.12
662	2.57	1513.21
669	0.89	1519.15
683	0.57	1522.94
686	10.38	1591.98
690	0.40	1594.64
697	2.12	1608.74
705	1.06	1615.79
711	0.35	1618.12

*Date of loading was September 14, 1979.
**Tap Water Addition.
***Storms of more than one day's duration were measured and recorded on the final day. Each cm of moisture was equivalent to 6.65 liters of water.

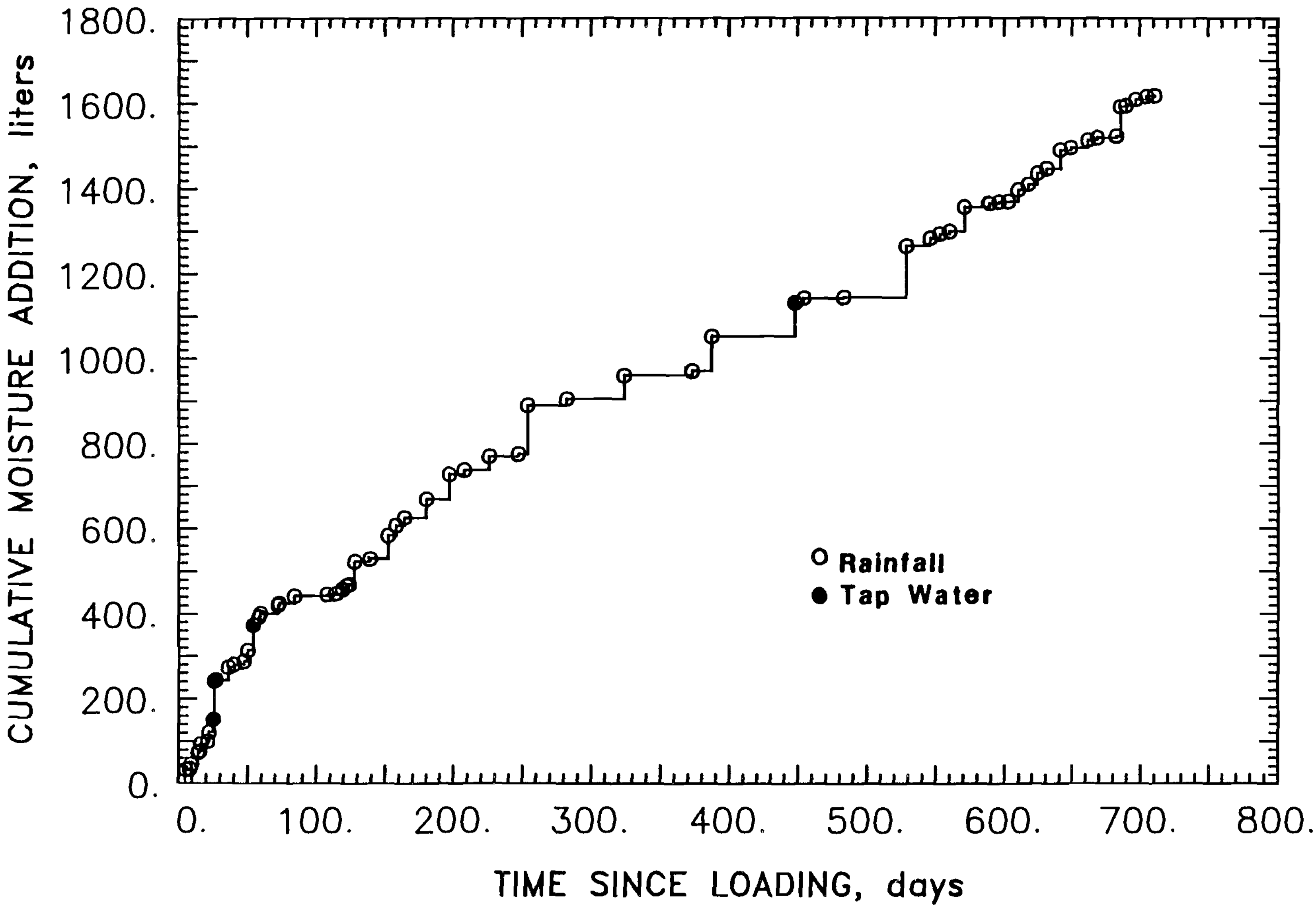


Figure 12. Cumulative Moisture Addition as Rainfall or Tap Water

TABLE 13. LEACHATE ANALYSIS FROM COLUMN 1

Time Since Loading, day	35	47	72	86	93
Chemical Oxygen Demand, mg/L	10800	11740	7290	6700	6780
Biochemical Oxygen Demand (BOD_5), mg/L	6700	5900			3750
pH	5.32	5.35	5.95		5.68
Alkalinity, mg/L as $CaCO_3$	1510		1600		1010
Conductivity, μmho/cm		6700	5300	3700	4900
Oxidation-Reduction Potential, mV E_c				-100	
Acetic Acid, mg/L					667
Propionic Acid, mg/L					287
Isobutyric Acid, mg/L					BDL
Butyric Acid, mg/L					131
Total Volatile Acids, mg/L as acetic acid					989
Aromatic Hydroxyl, mg/L as tannic acid	213	331	339	96	258
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	88	100	105	54	83
Ammonia, mg/L as N	58	54	58	56	44
Orthophosphate, mg/L as P	9.8	8.2	7.5	1.4	3.9
Chlorides, mg/L			630	620	610
Sulfides, mg/L					1.2
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L		BDL	BDL		
Calcium, mg/L		425	400		
Chromium, mg/L	BDL	BDL	BDL		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L		100	88		
Manganese, mg/L		8.6	8.6		
Magnesium, mg/L		290	250		
Nickel, mg/L		BDL	BDL		
Sodium, mg/L		840	750		
Potassium, mg/L		450	450		
Zinc, mg/L		0.75	0.7		

TABLE 13 (continued)

Time Since Loading, day	102	108	114	128	150
Chemical Oxygen Demand, mg/L			6620	2370	1630
Biochemical Oxygen Demand (BOD_5), mg/L					
pH		6.54	6.42	6.69	7.04
Alkalinity, mg/L as $CaCO_3$		1170	1750	1180	
Conductivity, µmho/cm	3700	4300			2700
Oxidation-Reduction Potential, mV E_c					
Acetic Acid, mg/L			368		
Propionic Acid, mg/L			245		
Isobutyric Acid, mg/L			BDL		
Butyric Acid, mg/L			180		
Total Volatile Acids, mg/L as acetic acid			689		
Aromatic Hydroxyl, mg/L as tannic acid	178	219	199	42	10
Carbohydrate, mg/L as glucose			243		110
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	51	53	64	34	34
Ammonia, mg/L as N	33	25	19	6	6
Orthophosphate, mg/L as P	0.6	0.7	1.2	1.1	0.4
Chlorides, mg/L	630	630	620	480	480
Sulfides, mg/L					2.5
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	650	350	300	250	290
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	80	50	38	11	12
Manganese, mg/L	7.8	8.2	8.0	6.2	7.6
Magnesium, mg/L	280	270	250	100	90
Nickel, mg/L	BDL	BDL	0.25	T	T
Sodium, mg/L	780	710	710	470	380
Potassium, mg/L	425	375	360	230	190
Zinc, mg/L	0.75	0.70	0.88	0.8	0.61

TABLE 13 (continued)

Time Since Loading, day	153	164	179	197	211
Chemical Oxygen Demand, mg/L	3700	2091		2660	1750
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.49	7.01	6.42	6.62	6.71
Alkalinity, mg/L as $CaCO_3$		1460	1100	1880	1110
Conductivity, μmho/cm		3000	2450	2220	2250
Oxidation-Reduction Potential, mV E_c		-30	-65		-65
Acetic Acid, mg/L		250			145
Propionic Acid, mg/L		80			287
Isobutyric Acid, mg/L		BDL			BDL
Butyric Acid, mg/L		30			20
Total Volatile Acids, mg/L as acetic acid		335			391
Aromatic Hydroxyl, mg/L as tannic acid		39	44	52	66
Carbohydrate, mg/L as glucose		96	173	135	99
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		33	28	21	22
Ammonia, mg/L as N		6	5		3
Orthophosphate, mg/L as P		0.3	0.3		0.6
Chlorides, mg/L		490	440	380	400
Sulfides, mg/L			BDL		0.19
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L			BDL		BDL
Calcium, mg/L			150		110
Chromium, mg/L			BDL	BDL	BDL
Copper, mg/L			BDL	BDL	BDL
Iron, mg/L			40		41
Manganese, mg/L			8.2		8.0
Magnesium, mg/L			110		90
Nickel, mg/L			BDL		BDL
Sodium, mg/L			410		340
Potassium, mg/L			220		180
Zinc, mg/L			4.5		0.8

TABLE 13 (continued)

Time Since Loading, day	224	226	233	240	247
Chemical Oxygen Demand, mg/L	1536	1637	1619	1650	1130
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.58	6.60	6.57	6.40	
Alkalinity, mg/L as $CaCO_3$	1120	1120	1120	1330	
Conductivity, μmho/cm	2400	2300		2650	2750
Oxidation-Reduction Potential, mV E_c			-85	-89	
Acetic Acid, mg/L	99				
Propionic Acid, mg/L	303				
Isobutyric Acid, mg/L	6				
Butyric Acid, mg/L	6				
Total Volatile Acids, mg/L as acetic acid	353				
Aromatic Hydroxyl, mg/L as tannic acid	60	62	38	46	71
Carbohydrate, mg/L as glucose	120	123	56	87	83
Carboxyl, mg/L as acetic acid			395		365
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	16	22	23	32	37
Ammonia, mg/L as N	2		3	6	6
Orthophosphate, mg/L as P	0.2	0.4	0.6	0.9	1.7
Chlorides, mg/L	390	390		430	415
Sulfides, mg/L				0.58	
Total Solids, mg/L			3210	3050	3020
Total Volatile Solids, mg/L			1710	1610	1730
Total Suspended Solids, mg/L			204	190	163
Volatile Suspended Solids, mg/L			103	91	101
Total Dissolved Solids, mg/L			3006	2860	2857
Volatile Dissolved Solids, mg/L			1607	1519	1692
Cadmium, mg/L		BDL	BDL	BDL	BDL
Calcium, mg/L		675	200	210	200
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L		22	30	40	42
Manganese, mg/L		6.2	7.5	8.1	8.1
Magnesium, mg/L		70	120	90	98
Nickel, mg/L		0.09	BDL	BDL	BDL
Sodium, mg/L		440	250	300	300
Potassium, mg/L		170	210	220	250
Zinc, mg/L		BDL	0.5	0.7	0.65

TABLE 13 (continued)

Time Since Loading, day	254	261	268	273	282
Chemical Oxygen Demand, mg/L	969	1156	1384	1231	1065
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.46	6.95	6.62	6.47	6.65
Alkalinity, mg/L as $CaCO_3$	463	372	320	340	310
Conductivity, μmho/cm			2750	2500	
Oxidation-Reduction Potential, mV E_c	-54	-93	-182	-95	-400
Acetic Acid, mg/L				220	
Propionic Acid, mg/L				BDL	
Isobutyric Acid, mg/L				33	
Butyric Acid, mg/L				40	
Total Volatile Acids, mg/L as acetic acid				270	
Aromatic Hydroxyl, mg/L as tannic acid	49	53	15	43	54
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid				855	
Protein, mg/L as leucine					
Total Carbon, mg/L	783	697	609	635	620
Total Organic Carbon, mg/L	463	372	320	340	310
Total Inorganic Carbon, mg/L	320	325	289	295	310
Total Kjeldahl Nitrogen, mg/L as N	31	34	32	34	44
Ammonia, mg/L as N	6	6	6	5	6
Orthophosphate, mg/L as P	0.8	1.1	1.6	1.2	2.1
Chlorides, mg/L			390	400	
Sulfides, mg/L	0.5	0.15	0.13	0.55	0.18
Total Solids, mg/L	3010	3000	2970	2900	2860
Total Volatile Solids, mg/L	1110	1150	1100	1070	1040
Total Suspended Solids, mg/L	147	142	135	123	122
Volatile Suspended Solids, mg/L	73	76	75	74	77
Total Dissolved Solids, mg/L	2863	2858	2835	2777	2738
Volatile Dissolved Solids, mg/L	1037	1074	1025	996	963
Cadmium, mg/L	BDL	BDL	BDL		
Calcium, mg/L	150	150	175	250	
Chromium, mg/L	BDL	BDL	BDL	BDL	
Copper, mg/L	BDL	BDL	BDL	BDL	
Iron, mg/L	38	42	30	38	
Manganese, mg/L	7.5	7.2	6.4	6.4	
Magnesium, mg/L	100	200	140	150	
Nickel, mg/L	0.06	0.11	0.11	BDL	
Sodium, mg/L	260	325	300	250	
Potassium, mg/L	250	270	260	270	
Zinc, mg/L	BDL	BDL	0.5	BDL	

TABLE 13 (continued)

Time Since Loading, day	289	298	303	310	318
Chemical Oxygen Demand, mg/L	1124	890		930	1008
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.62	6.62	6.65	6.95	
Alkalinity, mg/L as $CaCO_3$	325	250	400	1420	
Conductivity, µmho/cm	2650	2900	2900	2050	3000
Oxidation-Reduction Potential, mV E_c	-195		-380	-147	
Acetic Acid, mg/L				231	88
Propionic Acid, mg/L				BDL	413
Isobutyric Acid, mg/L				BDL	BDL
Butyric Acid, mg/L				BDL	BDL
Total Volatile Acids, mg/L as acetic acid				231	423
Aromatic Hydroxyl, mg/L as tannic acid	10	12	11	10	16
Carbohydrate, mg/L as glucose				57	51
Carboxyl, mg/L as acetic acid			580		
Protein, mg/L as leucine					
Total Carbon, mg/L	645	565	735	750	777
Total Organic Carbon, mg/L	325	250	400	420	447
Total Inorganic Carbon, mg/L	320	315	335	330	330
Total Kjeldahl Nitrogen, mg/L as N	48	44	61	68	71
Ammonia, mg/L as N	6	6	5	5	5
Orthophosphate, mg/L as P	2.3	2.4	2.4	2.5	2.5
Chlorides, mg/L			420	370	450
Sulfides, mg/L	0.28				0.07
Total Solids, mg/L	2660	2710	2810	2830	2930
Total Volatile Solids, mg/L	827	975	1010	1100	1103
Total Suspended Solids, mg/L	37	58	72	92	103
Volatile Suspended Solids, mg/L	30	46	54	77	80
Total Dissolved Solids, mg/L	2623	2652	2738	2738	2827
Volatile Dissolved Solids, mg/L	797	929	956	1023	1023
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	200	225	200	390	150
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	40	50	50	38	40
Manganese, mg/L	4.8	3.6	3.8	3.0	2.6
Magnesium, mg/L	130	110	110	140	110
Nickel, mg/L	0.14	0.9	0.06	0.06	0.08
Sodium, mg/L	250	290	305	260	335
Potassium, mg/L	300	310	310	350	330
Zinc, mg/L					

TABLE 13 (continued)

Time Since Loading, day	324	331	338	345	352
Chemical Oxygen Demand, mg/L	891	1341	950	1111	1250
Biochemical Oxygen Demand (BOD_5), mg/L	450	900	550	610	750
pH	6.89	6.66	6.59	6.45	6.82
Alkalinity, mg/L as $CaCO_3$	1420	830	1300	1360	1360
Conductivity, µmho/cm	3000	3050	3250		3500
Oxidation-Reduction Potential, mV E_c	-108	-275	-125	-130	-140
Acetic Acid, mg/L	BDL	47	35	130	
Propionic Acid, mg/L	BDL	BDL	BDL	BDL	
Isobutyric Acid, mg/L	BDL	BDL	BDL	BDL	
Butyric Acid, mg/L	BDL	BDL	BDL	BDL	
Total Volatile Acids, mg/L as acetic acid	BDL	47	35	130	
Aromatic Hydroxyl, mg/L as tannic acid	21	22	22	19	10
Carbohydrate, mg/L as glucose	113	72	68	46	64
Carboxyl, mg/L as acetic acid		790			770
Protein, mg/L as leucine					
Total Carbon, mg/L	800	875	700	580	700
Total Organic Carbon, mg/L	475	575	425	290	450
Total Inorganic Carbon, mg/L	325	300	275	290	250
Total Kjeldahl Nitrogen, mg/L as N	72	73	70	75	74
Ammonia, mg/L as N	5	4	3	5	4
Orthophosphate, mg/L as P	2.6	2.7	2.8	2.8	2.9
Chlorides, mg/L	440		460		485
Sulfides, mg/L	3.3			0.25	
Total Solids, mg/L	2820	2670	2555	2300	2330
Total Volatile Solids, mg/L	998	1006	935	960	957
Total Suspended Solids, mg/L	97	107	114	119	100
Volatile Suspended Solids, mg/L	76	88	89	99	90
Total Dissolved Solids, mg/L	2723	2563	2441	2181	2230
Volatile Dissolved Solids, mg/L	992	918	846	861	867
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	225	200	625	225	625
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	36	39	40	45	63
Manganese, mg/L	2.6	2.0	2.4	2.9	2.6
Magnesium, mg/L	120	100	60	75	75
Nickel, mg/L	0.08	0.13	0.11	0.10	0.13
Sodium, mg/L	300	250	225	290	480
Potassium, mg/L	330	360	375	365	400
Zinc, mg/L	0.8	BDL	BDL	BDL	0.8

TABLE 13 (continued)

Time Since Loading, day	359	367	374	381	387
Chemical Oxygen Demand, mg/L	1036	1110	1000	1200	1150
Biochemical Oxygen Demand (BOD_5), mg/L	550	635	610	680	600
pH	6.71		6.75	6.57	
Alkalinity, mg/L as $CaCO_3$	1300			1480	
Conductivity, μmho/cm	3450		3350	3550	3400
Oxidation-Reduction Potential, mV E_c			-260	-290	
Acetic Acid, mg/L				BDL	
Propionic Acid, mg/L				BDL	
Isobutyric Acid, mg/L				BDL	
Butyric Acid, mg/L				BDL	
Total Volatile Acids, mg/L as acetic acid				BDL	
Aromatic Hydroxyl, mg/L as tannic acid	12		13		18
Carbohydrate, mg/L as glucose	77	89	38		
Carboxyl, mg/L as acetic acid					810
Protein, mg/L as leucine					
Total Carbon, mg/L	675	680	650	662	650
Total Organic Carbon, mg/L	325	400	350	377	362
Total Inorganic Carbon, mg/L	350	270	300	285	285
Total Kjeldahl Nitrogen, mg/L as N	78	75	69	75	73
Ammonia, mg/L as N	5	5	5	5	5
Orthophosphate, mg/L as P	3.0	3.0	2.9	3.0	2.9
Chlorides, mg/L	515		545	500	510
Sulfides, mg/L			0.11		
Total Solids, mg/L	2450	2500	2100	2210	2390
Total Volatile Solids, mg/L	1025	830	893	850	705
Total Suspended Solids, mg/L	99	109	116	114	115
Volatile Suspended Solids, mg/L	95	78	93	88	92
Total Dissolved Solids, mg/L	2351	2391	1984	2096	2275
Volatile Dissolved Solids, mg/L	930	752	800	762	613
Cadmium, mg/L	BDL		BDL	BDL	
Calcium, mg/L	425		500	225	
Chromium, mg/L	BDL	BDL	BDL	BDL	
Copper, mg/L	BDL	BDL	BDL	BDL	
Iron, mg/L	50		30	50	
Manganese, mg/L	2.6		2.5	2.5	
Magnesium, mg/L	60		60	75	
Nickel, mg/L	0.13		0.73	0.15	
Sodium, mg/L	470		350	360	
Potassium, mg/L	375		350	360	
Zinc, mg/L	BDL		BDL	0.06	

TABLE 13 (continued)

Time Since Loading, day	483	490	529	539	546
Chemical Oxygen Demand, mg/L	713		429	546	696
Biochemical Oxygen Demand (BOD_5), mg/L	390		225	280	350
pH	6.96		6.95	6.85	6.92
Alkalinity, mg/L as $CaCO_3$	1440		726	880	935
Conductivity, µmho/cm			3310	3310	3440
Oxidation-Reduction Potential, mV E_c	+16		+50	+39	+27
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid			13	12	19
Carbohydrate, mg/L as glucose			65	47	51
Carboxyl, mg/L as acetic acid			19	BDL	25
Protein, mg/L as leucine			70	50	
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	13		19	13	13
Ammonia, mg/L as N			14	12	9
Orthophosphate, mg/L as P			0.1		0.1
Chlorides, mg/L	445		431	455	439
Sulfides, mg/L					
Total Solids, mg/L	2347		2302	2490	2500
Total Volatile Solids, mg/L	603		958	1864	896
Total Suspended Solids, mg/L	121		106	99	110
Volatile Suspended Solids, mg/L	87		75	32	36
Total Dissolved Solids, mg/L	2226		2196	2391	2390
Volatile Dissolved Solids, mg/L	516		883	1832	860
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	353		285	315	405
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	45		30	75	75
Manganese, mg/L	2.1		1.8	2.8	3.0
Magnesium, mg/L	108		75	102	108
Nickel, mg/L	0.05		0.25	0.43	0.50
Sodium, mg/L	540		555	465	465
Potassium, mg/L	420		300	345	405
Zinc, mg/L	3.0		2.75	2.75	2.3

TABLE 13 (continued)

Time Since Loading, day	553	560	571	575	582
Chemical Oxygen Demand, mg/L	555	524	544	617	638
Biochemical Oxygen Demand (BOD_5), mg/L	300	280	290	340	320
pH	6.87	6.92	6.18	7.07	7.25
Alkalinity, mg/L as $CaCO_3$	1015		986	1020	1072
Conductivity, μmho/cm	3590	3470	3880	3570	3700
Oxidation-Reduction Potential, mV E_c	+22	-66	-180	-166	-100
Acetic Acid, mg/L			10	25	
Propionic Acid, mg/L			BDL	BDL	
Isobutyric Acid, mg/L			BDL	BDL	
Butyric Acid, mg/L			BDL	BDL	
Total Volatile Acids, mg/L as acetic acid			10	25	
Aromatic Hydroxyl, mg/L as tannic acid		17	16	11	21
Carbohydrate, mg/L as glucose	59		68	44	52
Carboxyl, mg/L as acetic acid	BDL	100	BDL	327	364
Protein, mg/L as leucine					
Total Carbon, mg/L					319
Total Organic Carbon, mg/L					217
Total Inorganic Carbon, mg/L					102
Total Kjeldahl Nitrogen, mg/L as N	13	9	8	18	24
Ammonia, mg/L as N	8	56	13	15	21
Orthophosphate, mg/L as P	BDL	BDL	0.1	0.3	0.3
Chlorides, mg/L	439	474	463	463	463
Sulfides, mg/L					
Total Solids, mg/L	2492	2556	2496	2519	2507
Total Volatile Solids, mg/L	516	558	456	507	471
Total Suspended Solids, mg/L	122	166	252	156	143
Volatile Suspended Solids, mg/L	40	62	102	73	46
Total Dissolved Solids, mg/L	2370	2390	2244	2363	2364
Volatile Dissolved Solids, mg/L	476	496	354	434	425
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	405	405	481	594	481
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	50	50	55	60	63
Manganese, mg/L	3.0	2.8	3.4	3.1	2.8
Magnesium, mg/L	111	111	78	68	75
Nickel, mg/L	0.33	0.20	0.18	0.13	0.28
Sodium, mg/L	480	465	288	338	375
Potassium, mg/L	405	428	350	285	325
Zinc, mg/L	2.2	3.0	2.8	2.7	2.4

TABLE 13 (continued)

Time Since Loading, day	589	596	603	610	617
Chemical Oxygen Demand, mg/L	585	487	470	419	511
Biochemical Oxygen Demand (BOD_5), mg/L	300	250	250	214	260
pH	6.96	7.30	7.09	7.06	7.15
Alkalinity, mg/L as $CaCO_3$	1061	1093	1157	1137	1074
Conductivity, µmho/cm	3320	3450	3490	3540	3530
Oxidation-Reduction Potential, mV E_c	-78	-36	-114	-143	-151
Acetic Acid, mg/L	BDL	26			15
Propionic Acid, mg/L	BDL	BDL			30
Isobutyric Acid, mg/L	BDL	BDL			BDL
Butyric Acid, mg/L	BDL	BDL			BDL
Total Volatile Acids, mg/L as acetic acid	BDL	26			39
Aromatic Hydroxyl, mg/L as tannic acid	15	21	17	17	17
Carbohydrate, mg/L as glucose	56	59	38	122	65
Carboxyl, mg/L as acetic acid	336	373	282	305	
Protein, mg/L as leucine		BDL			408
Total Carbon, mg/L	588	336	312	360	344
Total Organic Carbon, mg/L		228	217	255	239
Total Inorganic Carbon, mg/L		108	95	105	105
Total Kjeldahl Nitrogen, mg/L as N	24	34	34	33	32
Ammonia, mg/L as N	19	28	24	25	26
Orthophosphate, mg/L as P	0.5	0.4	0.5	0.3	0.5
Chlorides, mg/L	502	514	512	524	529
Sulfides, mg/L					
Total Solids, mg/L	2493	2574			
Total Volatile Solids, mg/L	474	546			
Total Suspended Solids, mg/L	122	135			
Volatile Suspended Solids, mg/L	47	50			
Total Dissolved Solids, mg/L	2371	2028			
Volatile Dissolved Solids, mg/L	427	496			
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	488	525	431	494	512
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	70	71	70	70	75
Manganese, mg/L	2.4	2.4	2.4	1.8	2.1
Magnesium, mg/L	103	78	75	78	70
Nickel, mg/L	0.11	0.20	0.15	0.25	0.20
Sodium, mg/L	400	519	425	469	456
Potassium, mg/L	325	325	375	325	325
Zinc, mg/L	2.5	2.0	1.8	1.9	1.7

TABLE 13 (continued)

Time Since Loading, day	624	631	641	650	655
Chemical Oxygen Demand, mg/L	470	527	546	519	521
Biochemical Oxygen Demand (BOD_5), mg/L	253	270	280	260	260
pH	7.11	7.12	7.12	7.27	7.03
Alkalinity, mg/L as $CaCO_3$	1112	1146	1150	1148	1181
Conductivity, µmho/cm	3630	3710	3710	3660	3830
Oxidation-Reduction Potential, mV E_c	-164	-144	-155	-152	-142
Acetic Acid, mg/L	70	13	BDL		
Propionic Acid, mg/L	30	BDL	BDL		
Isobutyric Acid, mg/L	BDL	BDL	BDL		
Butyric Acid, mg/L	BDL	BDL	BDL		
Total Volatile Acids, mg/L as acetic acid	94	13	BDL		
Aromatic Hydroxyl, mg/L as tannic acid	25	24	36		
Carbohydrate, mg/L as glucose	132	31		71	60
Carboxyl, mg/L as acetic acid	325	193	355	410	345
Protein, mg/L as leucine	24	31	70	25	
Total Carbon, mg/L	240	416	392		516
Total Organic Carbon, mg/L	172	294	270		331
Total Inorganic Carbon, mg/L	68	122	122		185
Total Kjeldahl Nitrogen, mg/L as N		37	26	33	45
Ammonia, mg/L as N	3	31	40	44	47
Orthophosphate, mg/L as P	0.5	0.6	0.7	0.9	0.7
Chlorides, mg/L	480	535	493	517	554
Sulfides, mg/L					
Total Solids, mg/L				2634	2934
Total Volatile Solids, mg/L				517	640
Total Suspended Solids, mg/L				253	288
Volatile Suspended Solids, mg/L				71	97
Total Dissolved Solids, mg/L				2381	2446
Volatile Dissolved Solids, mg/L				446	543
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	572	562	488	550	375
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	75	75	75	75	75
Manganese, mg/L	2.5	2.8	2.8	1.9	1.8
Magnesium, mg/L	70	88	70	78	63
Nickel, mg/L	0.15	0.10	0.10	0.10	0.15
Sodium, mg/L	400	550	469	550	435
Potassium, mg/L	350	438	350	375	375
Zinc, mg/L	1.6	1.6	1.5	1.4	1.4

TABLE 13 (continued)

Time Since Loading, day	662	669	676	683	686
Chemical Oxygen Demand, mg/L	528	526	586	551	380
Biochemical Oxygen Demand (BOD_5), mg/L		260	290	273	200
pH	7.10	7.08	6.88	7.06	6.62
Alkalinity, mg/L as $CaCO_3$	1158	1178	1293	1219	1092
Conductivity, μmho/cm	3500	4200	4400		3500
Oxidation-Reduction Potential, mV E_c	-117	-151	-130	-153	-101
Acetic Acid, mg/L	40	BDL	BDL	BDL	154
Propionic Acid, mg/L	25	BDL	BDL	BDL	148
Isobutyric Acid, mg/L	6	BDL	BDL	BDL	BDL
Butyric Acid, mg/L	23	BDL	BDL	BDL	28
Total Volatile Acids, mg/L as acetic acid	80	BDL	BDL	BDL	293
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					67
Protein, mg/L as leucine	218		236		
Total Carbon, mg/L	514	540	517	504	
Total Organic Carbon, mg/L	328	347	308	405	
Total Inorganic Carbon, mg/L	186	193	209	99	
Total Kjeldahl Nitrogen, mg/L as N	32	37	63	68	52
Ammonia, mg/L as N	47		51	47	45
Orthophosphate, mg/L as P	0.6	1.1	2.4	2.2	2.2
Chlorides, mg/L	538	543		563	418
Sulfides, mg/L					
Total Solids, mg/L			2549	2650	
Total Volatile Solids, mg/L			494	530	
Total Suspended Solids, mg/L			383	359	
Volatile Suspended Solids, mg/L			201	102	
Total Dissolved Solids, mg/L			2166	2291	
Volatile Dissolved Solids, mg/L			293	428	
Cadmium, mg/L	BDL	BDL	BDL	BDL	BDL
Calcium, mg/L	400	150	75	25	
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	75	70	75	75	52
Manganese, mg/L	2.0	1.6	1.8	1.6	BDL
Magnesium, mg/L	90	63	15	10	BDL
Nickel, mg/L	0.25	0.25	0.25	0.25	0.25
Sodium, mg/L	500	500	500	600	BDL
Potassium, mg/L	413	425	438	450	BDL
Zinc, mg/L	1.6	1.0	1.0	BDL	6.1

TABLE 13 (continued)

Time Since Loading, day	690	697	705	711	718
Chemical Oxygen Demand, mg/L	431	410	531	879	
Biochemical Oxygen Demand (BOD_5), mg/L	210	200	267		
pH	6.68	6.92	6.86	6.97	
Alkalinity, mg/L as $CaCO_3$	1017	1040	1174	1112	
Conductivity, µmho/cm	3800	3800	3800	4200	
Oxidation-Reduction Potential, mV E_c	-98	-107	-90		
Acetic Acid, mg/L	83	26	BDL	BDL	
Propionic Acid, mg/L	BDL	BDL	BDL	BDL	
Isobutyric Acid, mg/L	BDL	BDL	BDL	BDL	
Butyric Acid, mg/L	BDL	BDL	BDL	BDL	
Total Volatile Acids, mg/L as acetic acid	83	26	BDL	BDL	
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	BDL	BDL			
Protein, mg/L as leucine		227			
Total Carbon, mg/L	408	448	335	407	
Total Organic Carbon, mg/L	276	288	200	272	
Total Inorganic Carbon, mg/L	132	160	135	135	
Total Kjeldahl Nitrogen, mg/L as N	51	44	43	45	
Ammonia, mg/L as N	41	35	69	35	
Orthophosphate, mg/L as P	0.2	2.5	0.3	2.6	
Chlorides, mg/L	490	526	538	550	
Sulfides, mg/L				2430	
Total Solids, mg/L				834	
Total Volatile Solids, mg/L				112	
Total Suspended Solids, mg/L				42	
Volatile Suspended Solids, mg/L				2318	
Total Dissolved Solids, mg/L				792	
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	BDL	BDL	BDL	BDL	
Calcium, mg/L					
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	31	31	61	52	
Manganese, mg/L	BDL	BDL	BDL	BDL	
Magnesium, mg/L	BDL	BDL	BDL	BDL	
Nickel, mg/L	0.25	0.25	0.25	0.31	
Sodium, mg/L					
Potassium, mg/L					
Zinc, mg/L	2.2	3.0	5.1	3.8	

TABLE 14. LEACHATE ANALYSIS FROM COLUMN 2

Time Since Loading, day	35	47	72	86	93
Chemical Oxygen Demand, mg/L	19300	20830	13920	13790	13370
Biochemical Oxygen Demand (BOD_5), mg/L	12500	10400			8200
pH	5.32	5.77	5.61		5.45
Alkalinity, mg/L as $CaCO_3$	2120		2420		1190
Conductivity, µmho/cm		8800	7200	6900	7000
Oxidation-Reduction Potential, mV E_c				-80	
Acetic Acid, mg/L					574
Propionic Acid, mg/L					502
Isobutyric Acid, mg/L					BDL
Butyric Acid, mg/L					498
Total Volatile Acids, mg/L as acetic acid					1321
Aromatic Hydroxyl, mg/L as tannic acid	244	128	224	148	183
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	132	100	109	96	109
Ammonia, mg/L as N	16	9	8	8	8
Orthophosphate, mg/L as P	0.3	0.3	1.0	0.3	0.7
Chlorides, mg/L			820	810	810
Sulfides, mg/L					0.3
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	1.3	5.0	8.0		
Calcium, mg/L					
Chromium, mg/L	0.8	0.5	0.1		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L	120	116	118		
Manganese, mg/L	10.6	10.4	10.4		
Magnesium, mg/L	430	280	250		
Nickel, mg/L	1.0	1.0	1.0		
Sodium, mg/L	890	900	860		
Potassium, mg/L	500	450	430		
Zinc, mg/L		500	500		

TABLE 14 (continued)

Time Since Loading, day	102	108	114	128	150
Chemical Oxygen Demand, mg/L			13970	12630	7010
Biochemical Oxygen Demand (BOD_5), mg/L					
pH		5.92	5.92	5.96	6.97
Alkalinity, mg/L as $CaCO_3$		2140	2270	1420	
Conductivity, µmho/cm	7000	6750	7000	6300	5500
Oxidation-Reduction Potential, mV E_c					
Acetic Acid, mg/L			494		
Propionic Acid, mg/L			515		
Isobutyric Acid, mg/L			BDL		
Butyric Acid, mg/L			685		
Total Volatile Acids, mg/L as acetic acid			1379		
Aromatic Hydroxyl, mg/L as tannic acid	192	162	148	121	27
Carbohydrate, mg/L as glucose			185		141
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	99	93	99	73	83
Ammonia, mg/L as N	7	7	7	7	7
Orthophosphate, mg/L as P	0.4	0.3	0.3	0.2	0.3
Chlorides, mg/L	790	805	820	720	680
Sulfides, mg/L					0.02
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	4.0	3.0	3.0	1.9	0.9
Calcium, mg/L	550		450	280	420
Chromium, mg/L	0.1	T	0.2	T	T
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	88	92	80	40	13
Manganese, mg/L	9.6	10.0	9.8	8.8	7.0
Magnesium, mg/L	230	240	120	200	90
Nickel, mg/L	1.1	1.1	1.0	0.87	0.68
Sodium, mg/L	810	800	1000	610	560
Potassium, mg/L	460	450	420	310	290
Zinc, mg/L	500	500	425	275	185

TABLE 14 (continued)

Time Since Loading, day	153	164	179	197	211
Chemical Oxygen Demand, mg/L	8829	6225		1700	1275
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.74	6.83	6.86	6.82	7.31
Alkalinity, mg/L as $CaCO_3$		1950	1890	1460	1360
Conductivity, µmho/cm		5500	3400	2900	3150
Oxidation-Reduction Potential, mV E_c		-40	-75		-20
Acetic Acid, mg/L		210			218
Propionic Acid, mg/L		200			518
Isobutyric Acid, mg/L		BDL			BDL
Butyric Acid, mg/L		250			9
Total Volatile Acids, mg/L as acetic acid		540			644
Aromatic Hydroxyl, mg/L as tannic acid		79	57	24	28
Carbohydrate, mg/L as glucose		150	116	69	55
Carboxyl, mg/L as acetic acid			40		
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		79	71	64	45
Ammonia, mg/L as N		7	6		6
Orthophosphate, mg/L as P		0.3	0.2		0.1
Chlorides, mg/L		685		530	530
Sulfides, mg/L					
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L			0.5		0.25
Calcium, mg/L			320	190	
Chromium, mg/L			BDL	BDL	BDL
Copper, mg/L			BDL	BDL	BDL
Iron, mg/L			11		20
Manganese, mg/L			4.8		1.9
Magnesium, mg/L			75		160
Nickel, mg/L			0.25		0.25
Sodium, mg/L			500		560
Potassium, mg/L			270		320
Zinc, mg/L			50		13

TABLE 14 (continued)

Time Since Loading, day	224	226	233	240	247
Chemical Oxygen Demand, mg/L	1107	1091	2227	2320	2015
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.74	6.74	6.73	6.64	
Alkalinity, mg/L as $CaCO_3$	1410	1120	1300	1330	
Conductivity, μmho/cm	3300	3400		3400	3500
Oxidation-Reduction Potential, mV E_c			-90	-86	
Acetic Acid, mg/L	94				
Propionic Acid, mg/L	BDL				
Isobutyric Acid, mg/L	6				
Butyric Acid, mg/L	11				
Total Volatile Acids, mg/L as acetic acid	110				
Aromatic Hydroxyl, mg/L as tannic acid	76	66	48	66	78
Carbohydrate, mg/L as glucose	83	87	92		73
Carboxyl, mg/L as acetic acid		295	345		390
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	53	68	81	63	53
Ammonia, mg/L as N	7		7	6	6
Orthophosphate, mg/L as P	0.2	0.2	0.2	0.2	0.3
Chlorides, mg/L	540	540	555	580	540
Sulfides, mg/L			0.05	0.23	
Total Solids, mg/L			5610	5010	4810
Total Volatile Solids, mg/L			3020	3020	2030
Total Suspended Solids, mg/L			193	183	152
Volatile Suspended Solids, mg/L			89	87	73
Total Dissolved Solids, mg/L			5417	4827	4658
Volatile Dissolved Solids, mg/L			2931	2933	1957
Cadmium, mg/L		0.26	0.25	0.25	0.25
Calcium, mg/L		2000	200	210	210
Chromium, mg/L	BDL	T	BDL	0.1	6.3
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L		14	21	20	30
Manganese, mg/L		2.3	2.5	2.1	2.0
Magnesium, mg/L		58	98	70	70
Nickel, mg/L		0.40	0.25	0.31	0.31
Sodium, mg/L		330	290	320	320
Potassium, mg/L		220	300	290	300
Zinc, mg/L			37	32	32

TABLE 14 (continued)

Time Since Loading, day	254	261	268	273	282
Chemical Oxygen Demand, mg/L	1845	2130	2589	3362	4306
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.68	7.12	6.55	6.45	6.26
Alkalinity, mg/L as $CaCO_3$	588	675	700	980	1000
Conductivity, µmho/cm		4050	4850	3500	4350
Oxidation-Reduction Potential, mV E_c	-53	-55	-164	-50	-350
Acetic Acid, mg/L				990	
Propionic Acid, mg/L				495	
Isobutyric Acid, mg/L				77	
Butyric Acid, mg/L				236	
Total Volatile Acids, mg/L as acetic acid				1650	
Aromatic Hydroxyl, mg/L as tannic acid	59	61	19	64	75
Carbohydrate, mg/L as glucose		89			
Carboxyl, mg/L as acetic acid	860			960	
Protein, mg/L as leucine					
Total Carbon, mg/L	643	738	750	1027	1059
Total Organic Carbon, mg/L	588	675	700	980	1000
Total Inorganic Carbon, mg/L	55	63	50	47	59
Total Kjeldahl Nitrogen, mg/L as N	45	46	50	52	55
Ammonia, mg/L as N	6	6	6	7	5
Orthophosphate, mg/L as P	0.2	0.2	0.5	0.6	1.0
Chlorides, mg/L		495	495	495	
Sulfides, mg/L	0.2	0.09	0.25	1.9	0.52
Total Solids, mg/L	4900	4860	4715	4685	4620
Total Volatile Solids, mg/L	2300	2275	2200	2205	2200
Total Suspended Solids, mg/L	132	135	130	120	115
Volatile Suspended Solids, mg/L	64	70	73	75	76
Total Dissolved Solids, mg/L	4768	4725	4585	4565	4505
Volatile Dissolved Solids, mg/L	2236	2205	2127	2130	2124
Cadmium, mg/L	0.20	0.20	0.15		
Calcium, mg/L	300	325	225		
Chromium, mg/L	T	T	T		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L	25	25	32		
Manganese, mg/L	2.4	2.8	2.6		
Magnesium, mg/L	142	45	160		
Nickel, mg/L	0.28	0.26	0.34		
Sodium, mg/L	375	350	450		
Potassium, mg/L	300	310	320		
Zinc, mg/L			31		

TABLE 14 (continued)

Time Since Loading, day	289	298	303	310	318
Chemical Oxygen Demand, mg/L	4721	5122		5300	6965
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.21		6.06	6.14	
Alkalinity, mg/L as $CaCO_3$	1625	1800	1660	2310	
Conductivity, μmho/cm	4550	4500	400	4700	4750
Oxidation-Reduction Potential, mV E_c	-125		-270	-40	
Acetic Acid, mg/L	1450			3000	2400
Propionic Acid, mg/L	450			1140	350
Isobutyric Acid, mg/L	BDL			40	20
Butyric Acid, mg/L	BDL			230	150
Total Volatile Acids, mg/L as acetic acid	1820			4120	2800
Aromatic Hydroxyl, mg/L as tannic acid	19	39	24	26	40
Carbohydrate, mg/L as glucose				192	188
Carboxyl, mg/L as acetic acid			770		
Protein, mg/L as leucine					
Total Carbon, mg/L	1695	1845	1710	1445	2070
Total Organic Carbon, mg/L	1625	1800	1660	1400	2020
Total Inorganic Carbon, mg/L	70	45	50	45	50
Total Kjeldahl Nitrogen, mg/L as N	82	57	100	89	100
Ammonia, mg/L as N	6	6	5	5	6
Orthophosphate, mg/L as P	1.0	1.0	1.1	1.2	1.2
Chlorides, mg/L			470	500	510
Sulfides, mg/L	0.28		0.06		
Total Solids, mg/L	4850	5100	5310	5590	4180
Total Volatile Solids, mg/L	2220	2480	2620	2870	2350
Total Suspended Solids, mg/L	34	70	98	130	103
Volatile Suspended Solids, mg/L	28	43	61	96	90
Total Dissolved Solids, mg/L	4816	5030	5212	5460	4077
Volatile Dissolved Solids, mg/L	2192	2437	2559	2774	2260
Cadmium, mg/L	0.20	0.15	0.19	0.19	0.15
Calcium, mg/L	1000	275	275	500	300
Chromium, mg/L	0.2	0.1	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	45	60	63	70	65
Manganese, mg/L	2.8	3.2	3.2	4.4	4.0
Magnesium, mg/L	110	120	90	90	75
Nickel, mg/L	0.48	0.37	0.48	0.50	0.50
Sodium, mg/L	460	300	370	400	380
Potassium, mg/L	360	400	380	350	400
Zinc, mg/L					

TABLE 14 (continued)

Time Since Loading, day	324	331	338	345	352
Chemical Oxygen Demand, mg/L	6832		3992		
Biochemical Oxygen Demand (BOD_5), mg/L	3020		2010		
pH	5.84		6.13		
Alkalinity, mg/L as $CaCO_3$	2250				
Conductivity, μmho/cm	4950				
Oxidation-Reduction Potential, mV E_c	-11		-30		
Acetic Acid, mg/L	2150				
Propionic Acid, mg/L	200				
Isobutyric Acid, mg/L	BDL				
Butyric Acid, mg/L	250				
Total Volatile Acids, mg/L as acetic acid	2600				
Aromatic Hydroxyl, mg/L as tannic acid	44				
Carbohydrate, mg/L as glucose	215				
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L	2300				
Total Organic Carbon, mg/L	2250				
Total Inorganic Carbon, mg/L	50				
Total Kjeldahl Nitrogen, mg/L as N	105				
Ammonia, mg/L as N	4				
Orthophosphate, mg/L as P	1.3				
Chlorides, mg/L	490				
Sulfides, mg/L	3.4				
Total Solids, mg/L	4760				
Total Volatile Solids, mg/L	2660				
Total Suspended Solids, mg/L	115				
Volatile Suspended Solids, mg/L	93				
Total Dissolved Solids, mg/L	4645				
Volatile Dissolved Solids, mg/L	2567				
Cadmium, mg/L	0.21				
Calcium, mg/L	325				
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	80				
Manganese, mg/L	4.6				
Magnesium, mg/L	60				
Nickel, mg/L	0.63				
Sodium, mg/L	370				
Potassium, mg/L	420				
Zinc, mg/L	100				

TABLE 14 (continued)

Time Since Loading, day	483	490	529	539	546
Chemical Oxygen Demand, mg/L			140	510	536
Biochemical Oxygen Demand (BOD_5), mg/L			72	250	270
pH			7.14	7.49	7.80
Alkalinity, mg/L as $CaCO_3$			660	814	605
Conductivity, μmho/cm			3310	3160	3160
Oxidation-Reduction Potential, mV E_c			+194	+108	+100
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid				11	11
Carbohydrate, mg/L as glucose				56	53
Carboxyl, mg/L as acetic acid				BDL	50
Protein, mg/L as leucine			BDL		
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N				13	8
Ammonia, mg/L as N				2	1
Orthophosphate, mg/L as P				BDL	BDL
Chlorides, mg/L			554	544	552
Sulfides, mg/L					
Total Solids, mg/L			2504	2206	2105
Total Volatile Solids, mg/L			2010	1764	670
Total Suspended Solids, mg/L			46	33	40
Volatile Suspended Solids, mg/L			20	14	16
Total Dissolved Solids, mg/L			2458	2173	2065
Volatile Dissolved Solids, mg/L			1990	1750	654
Cadmium, mg/L			0.2	0.1	0.1
Calcium, mg/L			270	300	330
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L			3	1.0	0.9
Manganese, mg/L			1.1	0.9	0.8
Magnesium, mg/L			70	47	47
Nickel, mg/L			0.25	0.25	0.70
Sodium, mg/L			555	525	503
Potassium, mg/L			255	315	308
Zinc, mg/L			53	25	23

TABLE 14 (continued)

Time Since Loading, day	553	560	571	575	582
Chemical Oxygen Demand, mg/L	525	508	418	514	514
Biochemical Oxygen Demand (BOD_5), mg/L	295	267	220	270	280
pH	7.76	7.41	7.05	7.40	7.34
Alkalinity, mg/L as $CaCO_3$	789		657	765	770
Conductivity, µmho/cm	3230	3270	3710	3490	3400
Oxidation-Reduction Potential, mV E_c	+85	-156	-112	+114	+64
Acetic Acid, mg/L			10	20	
Propionic Acid, mg/L			BDL	BDL	
Isobutyric Acid, mg/L			BDL	BDL	
Butyric Acid, mg/L			BDL	BDL	
Total Volatile Acids, mg/L as acetic acid			10	20	
Aromatic Hydroxyl, mg/L as tannic acid		9	9	9	9
Carbohydrate, mg/L as glucose	50	42	44	49	44
Carboxyl, mg/L as acetic acid	38	BDL	BDL	314	
Protein, mg/L as leucine				112	
Total Carbon, mg/L					252
Total Organic Carbon, mg/L					187
Total Inorganic Carbon, mg/L					65
Total Kjeldahl Nitrogen, mg/L as N	7	5	6	5	6
Ammonia, mg/L as N	4	11	3	1	1
Orthophosphate, mg/L as P	0.1	BDL	1.0	0.3	0.3
Chlorides, mg/L	527	571	536	536	548
Sulfides, mg/L					
Total Solids, mg/L	2170	2254	2156	2301	2234
Total Volatile Solids, mg/L	346	314	285	372	270
Total Suspended Solids, mg/L	46	22	50	41	36
Volatile Suspended Solids, mg/L	20	16	9	16	11
Total Dissolved Solids, mg/L	2124	2232	2106	2260	2198
Volatile Dissolved Solids, mg/L	326	298	276	356	259
Cadmium, mg/L	0.1	0.1	0.1	0.1	0.1
Calcium, mg/L	345	375	400	875	812
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	0.9	0.8	1.0	1.6	1.0
Manganese, mg/L	0.6	0.8	0.6	0.7	0.7
Magnesium, mg/L	47	55	50	55	45
Nickel, mg/L	0.25	0.20	0.13	0.13	0.28
Sodium, mg/L	525	540	325	444	400
Potassium, mg/L	345	420	300	269	300
Zinc, mg/L	23	30	29	31	31

TABLE 14 (continued)

Time Since Loading, day	589	596	603	610	617
Chemical Oxygen Demand, mg/L	423	442	416	308	436
Biochemical Oxygen Demand (BOD_5), mg/L	177		220	153	220
pH	8.10	8.41	8.37	8.42	7.62
Alkalinity, mg/L as $CaCO_3$	700	722	761	748	851
Conductivity, μmho/cm	3460	3020	3310	3240	3490
Oxidation-Reduction Potential, mV E_c	+154	+180	+94	+54	+60
Acetic Acid, mg/L	BDL	BDL			BDL
Propionic Acid, mg/L	BDL	BDL			BDL
Isobutyric Acid, mg/L	BDL	BDL			BDL
Butyric Acid, mg/L	BDL	BDL			BDL
Total Volatile Acids, mg/L as acetic acid	BDL	BDL			BDL
Aromatic Hydroxyl, mg/L as tannic acid	9	9	10	9	9
Carbohydrate, mg/L as glucose	33	38	40	31	18
Carboxyl, mg/L as acetic acid	327	300	336		280
Protein, mg/L as leucine		25			471
Total Carbon, mg/L	330	270	264	294	286
Total Organic Carbon, mg/L		198	205	209	206
Total Inorganic Carbon, mg/L		72	59	85	80
Total Kjeldahl Nitrogen, mg/L as N	4	6	6	7	5
Ammonia, mg/L as N	1	0.5	1	1	0.5
Orthophosphate, mg/L as P	0.3	0.4	0.6	0.2	0.3
Chlorides, mg/L	575	575	586	604	616
Sulfides, mg/L					
Total Solids, mg/L	2136	2268			
Total Volatile Solids, mg/L	303	397			
Total Suspended Solids, mg/L		22			
Volatile Suspended Solids, mg/L		8			
Total Dissolved Solids, mg/L		2246			
Volatile Dissolved Solids, mg/L		389			
Cadmium, mg/L	0.04	0.04	0.04	0.03	0.06
Calcium, mg/L	425	425	538	488	550
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	0.8	1.1	1.0	0.6	0.6
Manganese, mg/L	0.7	0.6	0.5	0.5	0.7
Magnesium, mg/L	40	40	48	38	43
Nickel, mg/L	0.18	0.28	0.30	0.25	0.25
Sodium, mg/L	456	469	519	444	469
Potassium, mg/L	285	300	285	300	300
Zinc, mg/L	30	29	30	29	31

TABLE 14 (continued)

Time Since Loading, day	624	631	641	650	655
Chemical Oxygen Demand, mg/L	323	309	378	381	365
Biochemical Oxygen Demand (BOD_5), mg/L	200	150	200	200	180
pH	7.38	7.23	7.34	7.38	7.21
Alkalinity, mg/L as $CaCO_3$	868	862	839	904	921
Conductivity, µmho/cm	3400	3380	3360	3420	3600
Oxidation-Reduction Potential, mV E_c	+39	-42	-79	-95	+61
Acetic Acid, mg/L	BDL	15	BDL		
Propionic Acid, mg/L	BDL	BDL	BDL		
Isobutyric Acid, mg/L	BDL	BDL	BDL		
Butyric Acid, mg/L	BDL	BDL	BDL		
Total Volatile Acids, mg/L as acetic acid	BDL	15	BDL		
Aromatic Hydroxyl, mg/L as tannic acid	9	9	9		
Carbohydrate, mg/L as glucose	24	23	36	34	35
Carboxyl, mg/L as acetic acid		140	298	330	340
Protein, mg/L as leucine	49	32	26		
Total Carbon, mg/L	246	285	258		402
Total Organic Carbon, mg/L	174	199	170		257
Total Inorganic Carbon, mg/L	72	86	88		145
Total Kjeldahl Nitrogen, mg/L as N	6		5	6	6
Ammonia, mg/L as N	1	0.1	0.2	0.2	0.1
Orthophosphate, mg/L as P	0.3	0.4	0.6	0.6	0.6
Chlorides, mg/L	566	591	586	604	592
Sulfides, mg/L					
Total Solids, mg/L				2452	2487
Total Volatile Solids, mg/L				372	465
Total Suspended Solids, mg/L				56	12
Volatile Suspended Solids, mg/L				10	10
Total Dissolved Solids, mg/L				2396	2475
Volatile Dissolved Solids, mg/L				362	455
Cadmium, mg/L	0.06	0.07	0.08	0.06	0.08
Calcium, mg/L	525	356	300	856	894
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	1.0	2.0	2.3	2.8	2.8
Manganese, mg/L	0.7	0.8	0.7	0.8	0.9
Magnesium, mg/L	47	39	39	53	39
Nickel, mg/L	0.30	0.25	0.15	0.20	0.30
Sodium, mg/L	456	563	456	500	456
Potassium, mg/L	350	325	313	350	338
Zinc, mg/L	30	31	31	31	31

TABLE 14 (continued)

Time Since Loading, day	662	669	676	683	686
Chemical Oxygen Demand, mg/L	358	382	552	1702	970
Biochemical Oxygen Demand (BOD_5), mg/L		190	275		500
pH	7.17	7.10	6.74	6.76	6.46
Alkalinity, mg/L as $CaCO_3$	868	865	918	1085	773
Conductivity, μmho/cm	3900	4000	4100		3500
Oxidation-Reduction Potential, mV E_c	+32	-80	-81	-102	-96
Acetic Acid, mg/L	37	BDL	BDL	336	202
Propionic Acid, mg/L	19	BDL	BDL	202	87
Isobutyric Acid, mg/L	BDL	BDL	BDL	BDL	15
Butyric Acid, mg/L	18	BDL	BDL	BDL	BDL
Total Volatile Acids, mg/L as acetic acid	65	BDL	BDL	500	283
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					661
Protein, mg/L as leucine	286	200	226		
Total Carbon, mg/L	341	436	330	782	
Total Organic Carbon, mg/L	209	283	187	575	
Total Inorganic Carbon, mg/L	132	153	143	207	
Total Kjeldahl Nitrogen, mg/L as N	6	6	7		18
Ammonia, mg/L as N	0.1		0.2	8	2
Orthophosphate, mg/L as P	0.5	1.4	1.7	2.7	3.0
Chlorides, mg/L	522	546	571	583	515
Sulfides, mg/L					
Total Solids, mg/L			2561	3606	
Total Volatile Solids, mg/L			496	1011	
Total Suspended Solids, mg/L			183	152	
Volatile Suspended Solids, mg/L			130	76	
Total Dissolved Solids, mg/L			2378	3454	
Volatile Dissolved Solids, mg/L			366	935	
Cadmium, mg/L	0.05	0.08	0.09	0.13	0.09
Calcium, mg/L	450	100	25	25	
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	2.3	2.5	5	10	39
Manganese, mg/L	0.8	0.8	0.9	0.7	
Magnesium, mg/L	50	30	10	10	
Nickel, mg/L	0.38	0.5	0.5	0.62	0.38
Sodium, mg/L	550	525	550	700	
Potassium, mg/L	388	425	413	463	
Zinc, mg/L	25	16	25	100	35

TABLE 14 (continued)

Time Since Loading, day	690	697	705	711	718
Chemical Oxygen Demand, mg/L	1140	1492	2051	2200	1034
Biochemical Oxygen Demand (BOD_5), mg/L	573		1025		
pH	6.76	6.86	6.47	6.54	
Alkalinity, mg/L as $CaCO_3$	1066	1257	1457	1476	
Conductivity, µmho/cm	3600	4400	5000	4900	
Oxidation-Reduction Potential, mV E_c	-94	-70	-43	-67	
Acetic Acid, mg/L	228	418	460	298	264
Propionic Acid, mg/L	106	192	206	137	115
Isobutyric Acid, mg/L	BDL	BDL	BDL	BDL	BDL
Butyric Acid, mg/L	BDL	BDL	BDL	BDL	BDL
Total Volatile Acids, mg/L as acetic acid	314	574	627	409	357
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	400	3623			
Protein, mg/L as leucine		230			
Total Carbon, mg/L	576	760	747	864	
Total Organic Carbon, mg/L	480	640	693	784	
Total Inorganic Carbon, mg/L	96	120	54	80	
Total Kjeldahl Nitrogen, mg/L as N	11	15	20	22	15
Ammonia, mg/L as N	2	7	7	9	4
Orthophosphate, mg/L as P	7.2	3.1	2.7	2.9	2.8
Chlorides, mg/L	563	588	593	617	
Sulfides, mg/L					
Total Solids, mg/L				4102	
Total Volatile Solids, mg/L				1814	
Total Suspended Solids, mg/L				154	
Volatile Suspended Solids, mg/L				92	
Total Dissolved Solids, mg/L				3948	
Volatile Dissolved Solids, mg/L				1722	
Cadmium, mg/L	0.08	0.09	0.09	0.08	
Calcium, mg/L					
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	43	59	83	91	
Manganese, mg/L					
Magnesium, mg/L					
Nickel, mg/L	0.2	0.25	0.25	0.31	
Sodium, mg/L					
Potassium, mg/L					
Zinc, mg/L	38	46	50	75	37.5

TABLE 15. LEACHATE ANALYSIS FROM COLUMN 3

Time Since Loading, day	35	47	72	86	93
Chemical Oxygen Demand, mg/L		13450	9300	9000	8140
Biochemical Oxygen Demand (BOD_5), mg/L		6000			6400
pH		5.66	6.08		6.08
Alkalinity, mg/L as $CaCO_3$			1930	2230	1370
Conductivity, µmho/cm		6500	6500		6400
Oxidation-Reduction Potential, mV E_c				-90	
Acetic Acid, mg/L					352
Propionic Acid, mg/L					394
Isobutyric Acid, mg/L					BDL
Butyric Acid, mg/L					297
Total Volatile Acids, mg/L as acetic acid					673
Aromatic Hydroxyl, mg/L as tannic acid		104	103	44	82
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		109	99	105	93
Ammonia, mg/L as N	13	7	8		7
Orthophosphate, mg/L as P	0.3	0.3	0.3	0.3	0.3
Chlorides, mg/L			880	890	890
Sulfides, mg/L					0.3
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L		5.0	5.0		
Calcium, mg/L		500	500		
Chromium, mg/L	BDL	T	T		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L		210	200		
Manganese, mg/L		9.2	8.8		
Magnesium, mg/L		320	300		
Nickel, mg/L		0.8	0.6		
Sodium, mg/L		990	1010		
Potassium, mg/L		590	520		
Zinc, mg/L		270	250		

TABLE 15 (continued)

Time Since Loading, day	102	108	114	128	150
Chemical Oxygen Demand, mg/L			8820	20700	
Biochemical Oxygen Demand (BOD_5), mg/L					
pH		6.55	6.63	6.41	
Alkalinity, mg/L as $CaCO_3$		2090	2190	1600	
Conductivity, µmho/cm	6400	6300	6400	5600	
Oxidation-Reduction Potential, mV E_c					
Acetic Acid, mg/L			583		
Propionic Acid, mg/L			515		
Isobutyric Acid, mg/L			BDL		
Butyric Acid, mg/L			530		
Total Volatile Acids, mg/L as acetic acid			1390		
Aromatic Hydroxyl, mg/L as tannic acid	98	84	60	23	
Carbohydrate, mg/L as glucose			341	281	
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	93	89	83	82	
Ammonia, mg/L as N	7	6	7	8	
Orthophosphate, mg/L as P	0.3	0.2	0.4	0.5	
Chlorides, mg/L	910	930	920	790	795
Sulfides, mg/L					
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	2.5	2.5	1.8	1.2	1.0
Calcium, mg/L	400	400	280	120	100
Chromium, mg/L	BDL	BDL	BDL	T	T
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	110	75	69	38	40
Manganese, mg/L	7.6	7.4	6.8	4.8	4.0
Magnesium, mg/L	260	280	120	120	260
Nickel, mg/L	0.4	0.6	0.62	0.5	0.38
Sodium, mg/L	940	960	880	960	940
Potassium, mg/L	480	450	450	370	410
Zinc, mg/L	250	180	105	60	75

TABLE 15 (continued)

Time Since Loading, day	153	164	179	197	211
Chemical Oxygen Demand, mg/L	9108	6469		3830	4690
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	7.24	7.05	6.77	6.78	6.70
Alkalinity, mg/L as $CaCO_3$		2050	1790	1630	1890
Conductivity, µmho/cm		5200	3900	3800	4450
Oxidation-Reduction Potential, mV E_c		-45	-85		-65
Acetic Acid, mg/L		470			1090
Propionic Acid, mg/L		210			910
Isobutyric Acid, mg/L		BDL			BDL
Butyric Acid, mg/L		BDL			486
Total Volatile Acids, mg/L as acetic acid		680			2160
Aromatic Hydroxyl, mg/L as tannic acid		66	59	66	75
Carbohydrate, mg/L as glucose		339	366	247	341
Carboxyl, mg/L as acetic acid		1145			310
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		79	74	71	
Ammonia, mg/L as N		7	11		5
Orthophosphate, mg/L as P		0.8	0.5		0.3
Chlorides, mg/L		810	655	580	650
Sulfides, mg/L					0.05
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L			1.0		0.9
Calcium, mg/L			220	95	
Chromium, mg/L			BDL	BDL	BDL
Copper, mg/L			BDL	BDL	BDL
Iron, mg/L			25		50
Manganese, mg/L			3.8		2.9
Magnesium, mg/L			75		300
Nickel, mg/L			0.05		0.5
Sodium, mg/L			470		580
Potassium, mg/L			310		370
Zinc, mg/L			50		55

TABLE 15 (continued)

Time Since Loading, day	224	226	233	240	247
Chemical Oxygen Demand, mg/L	5520	5485	5617	5780	5580
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.61	6.60	6.40	6.50	
Alkalinity, mg/L as $CaCO_3$	1610	1800	1550	1850	
Conductivity, µmho/cm	4250	4300		5300	4750
Oxidation-Reduction Potential, mV E_c			-85	-67	
Acetic Acid, mg/L	890				
Propionic Acid, mg/L	430				
Isobutyric Acid, mg/L	50				
Butyric Acid, mg/L	510				
Total Volatile Acids, mg/L as acetic acid	1700				
Aromatic Hydroxyl, mg/L as tannic acid	74	95	92	103	89
Carbohydrate, mg/L as glucose	356	356		304	296
Carboxyl, mg/L as acetic acid	380		360	435	765
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	83	93	74	66	65
Ammonia, mg/L as N	7		6	6	7
Orthophosphate, mg/L as P	0.4	1.7	0.3	0.4	1.2
Chlorides, mg/L	615	610	655	640	600
Sulfides, mg/L			0.062	0.31	
Total Solids, mg/L			6510	6330	6250
Total Volatile Solids, mg/L			3280	2950	2950
Total Suspended Solids, mg/L			475	435	400
Volatile Suspended Solids, mg/L			229	209	187
Total Dissolved Solids, mg/L			6035	5895	5850
Volatile Dissolved Solids, mg/L			3051	2741	2763
Cadmium, mg/L		0.88	0.80	0.58	0.58
Calcium, mg/L		200	250	200	200
Chromium, mg/L	BDL	BDL	BDL	0.2	0.3
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L		70	88	100	100
Manganese, mg/L		2.8	3.3	2.8	2.8
Magnesium, mg/L		70	98	90	90
Nickel, mg/L		0.45	0.5	0.38	0.46
Sodium, mg/L		430	400	360	310
Potassium, mg/L		290	620	380	400
Zinc, mg/L			80	50	55

TABLE 15 (continued)

Time Since Loading, day	254	261	268	273	282
Chemical Oxygen Demand, mg/L	5489	6213	6607	6913	7685
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.30	6.71	6.21	6.18	6.03
Alkalinity, mg/L as $CaCO_3$	1400	2190	1710	1850	1800
Conductivity, μmho/cm		4350	4550	5300	
Oxidation-Reduction Potential, mV E_c	-22	-34	-140	-35	-250
Acetic Acid, mg/L				1100	
Propionic Acid, mg/L				200	
Isobutyric Acid, mg/L				BDL	
Butyric Acid, mg/L				BDL	
Total Volatile Acids, mg/L as acetic acid				1260	
Aromatic Hydroxyl, mg/L as tannic acid	89	86	19	85	101
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	1165	1010	620	2815	
Protein, mg/L as leucine					
Total Carbon, mg/L	1810	1670	1550	1660	2060
Total Organic Carbon, mg/L	1750	1615	1500	1600	2000
Total Inorganic Carbon, mg/L	60	55	50	60	60
Total Kjeldahl Nitrogen, mg/L as N	59	59	57	60	58
Ammonia, mg/L as N	7	6	5	5	5
Orthophosphate, mg/L as P	0.4	1.7	2.0	2.0	2.0
Chlorides, mg/L		540	540	555	
Sulfides, mg/L	0.2	0.05	0.03	0.5	0.12
Total Solids, mg/L	6200	6185	6150	6100	6110
Total Volatile Solids, mg/L	2980	2957	2980	3000	2960
Total Suspended Solids, mg/L	378	335	300	230	178
Volatile Suspended Solids, mg/L	107	103	102	98	93
Total Dissolved Solids, mg/L	5822	5850	5850	5870	5932
Volatile Dissolved Solids, mg/L	2873	2854	2878	2902	2867
Cadmium, mg/L	1.6	0.85	1.0		
Calcium, mg/L	200	225	200		
Chromium, mg/L	0.1	0.1	0.1		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L	100	110	106		
Manganese, mg/L	3.0	3.2	3.2		
Magnesium, mg/L	112	212	180		
Nickel, mg/L	0.48	0.57	0.65		
Sodium, mg/L	400	450	450		
Potassium, mg/L	375	450	450		
Zinc, mg/L			69		

TABLE 15 (continued)

Time Since Loading, day	289	298	303	310	318
Chemical Oxygen Demand, mg/L	8139			8455	10264
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.00			6.71	
Alkalinity, mg/L as $CaCO_3$	1760			3320	
Conductivity, µmho/cm	5950			6000	5750
Oxidation-Reduction Potential, mV E_c	-115			-85	
Acetic Acid, mg/L	1500			2400	2600
Propionic Acid, mg/L	1000			930	550
Isobutyric Acid, mg/L	BDL			110	50
Butyric Acid, mg/L	BDL			640	1150
Total Volatile Acids, mg/L as acetic acid	2400			3800	3864
Aromatic Hydroxyl, mg/L as tannic acid	36			53	37
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	1795			3900	7035
Protein, mg/L as leucine					
Total Carbon, mg/L	2430			1950	2460
Total Organic Carbon, mg/L	2380			1900	2410
Total Inorganic Carbon, mg/L	50			50	50
Total Kjeldahl Nitrogen, mg/L as N	78			112	115
Ammonia, mg/L as N	6			5	6
Orthophosphate, mg/L as P	2.0			2.0	2.1
Chlorides, mg/L					610
Sulfides, mg/L	0.10				
Total Solids, mg/L	8310			6840	6650
Total Volatile Solids, mg/L	2870			3500	4000
Total Suspended Solids, mg/L	105			185	215
Volatile Suspended Solids, mg/L	38			122	131
Total Dissolved Solids, mg/L	8205			6655	6435
Volatile Dissolved Solids, mg/L	2832			3378	3869
Cadmium, mg/L	1.25			1.5	1.23
Calcium, mg/L				250	250
Chromium, mg/L	0.2	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	105			125	120
Manganese, mg/L	4.0			5.2	5.8
Magnesium, mg/L	160			75	100
Nickel, mg/L	0.88			0.80	0.80
Sodium, mg/L	380			420	360
Potassium, mg/L	490			505	520
Zinc, mg/L					

TABLE 15 (continued)

Time Since Loading, day	324	331	338	345	352
Chemical Oxygen Demand, mg/L	10000	10728	9316	10972	10417
Biochemical Oxygen Demand (BOD_5), mg/L	5150	5500	4800	6580	6230
pH	5.84	5.78	5.73	5.60	5.94
Alkalinity, mg/L as $CaCO_3$	2960	2550	2430	3440	3200
Conductivity, µmho/cm	6050	6100	6400		7000
Oxidation-Reduction Potential, mV E_c	-20	-130	-25	-20	-40
Acetic Acid, mg/L	2100	3335	1800	2850	
Propionic Acid, mg/L	950	200	690	1120	
Isobutyric Acid, mg/L	BDL	180	100	BDL	
Butyric Acid, mg/L	250	710	530	BDL	
Total Volatile Acids, mg/L as acetic acid	3150	4920	2800	3750	
Aromatic Hydroxyl, mg/L as tannic acid	53	45	47	31	32
Carbohydrate, mg/L as glucose	467		275	163	160
Carboxyl, mg/L as acetic acid		8720	9050	6430	6710
Protein, mg/L as leucine					
Total Carbon, mg/L	2950	3000	2550	2850	3100
Total Organic Carbon, mg/L	2900	2920	2480	2780	3020
Total Inorganic Carbon, mg/L	50	80	70	70	80
Total Kjeldahl Nitrogen, mg/L as N	117	121	120	122	128
Ammonia, mg/L as N	4	4	4	4	3
Orthophosphate, mg/L as P	2.2	2.2	2.1	2.2	2.2
Chlorides, mg/L	590		620		625
Sulfides, mg/L	2.0			0.026	
Total Solids, mg/L	6500	5880	5800	5115	5010
Total Volatile Solids, mg/L	3500	3617	3600	3000	2990
Total Suspended Solids, mg/L	207	175	198	169	142
Volatile Suspended Solids, mg/L	123	117	104	99	106
Total Dissolved Solids, mg/L	6293	5705	5602	4946	4869
Volatile Dissolved Solids, mg/L	3377	3500	3496	2901	2884
Cadmium, mg/L	1.23	1.31	1.31	1.20	1.44
Calcium, mg/L	300	200	175	430	320
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	140	150	165	180	200
Manganese, mg/L	5.4	5.5	5.5	5.2	6.3
Magnesium, mg/L	90	75	90	130	80
Nickel, mg/L	0.71	0.83	0.76	0.33	1.08
Sodium, mg/L	410	375	375	385	510
Potassium, mg/L	520	560	540	555	570
Zinc, mg/L	150				150

TABLE 15 (continued)

Time Since Loading, day	359	367	374	381	387
Chemical Oxygen Demand, mg/L		9150		8800	
Biochemical Oxygen Demand (BOD_5), mg/L		4390		4580	
pH			5.21		
Alkalinity, mg/L as $CaCO_3$			2960	2580	
Conductivity, µmho/cm			6850		
Oxidation-Reduction Potential, mV E_c			-210		
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid			75		29
Carbohydrate, mg/L as glucose			232		211
Carboxyl, mg/L as acetic acid			4130		
Protein, mg/L as leucine					
Total Carbon, mg/L		2900		2650	
Total Organic Carbon, mg/L		2850		2580	
Total Inorganic Carbon, mg/L		50	80		
Total Kjeldahl Nitrogen, mg/L as N		125		127	
Ammonia, mg/L as N		3		5	
Orthophosphate, mg/L as P		2.3		2.3	
Chlorides, mg/L			710		
Sulfides, mg/L			0.017		
Total Solids, mg/L	4100		4500		
Total Volatile Solids, mg/L	2600		2010		
Total Suspended Solids, mg/L	151		162		
Volatile Suspended Solids, mg/L	115		125		
Total Dissolved Solids, mg/L	3949		4338		
Volatile Dissolved Solids, mg/L	2485		1885		
Cadmium, mg/L			0.89		
Calcium, mg/L			150		
Chromium, mg/L	BDL		BDL	BDL	
Copper, mg/L	BDL		BDL	BDL	
Iron, mg/L			140		
Manganese, mg/L					
Magnesium, mg/L			60		
Nickel, mg/L			0.73		
Sodium, mg/L			500		
Potassium, mg/L			510		
Zinc, mg/L			225	225	

TABLE 15 (continued)

Time Since Loading, day	483	490	529	539	546
Chemical Oxygen Demand, mg/L	5913		840	1092	1464
Biochemical Oxygen Demand (BOD_5), mg/L	3200		420	550	700
pH	6.80		6.96	6.68	6.70
Alkalinity, mg/L as $CaCO_3$	2790		1221	1078	2970
Conductivity, μmho/cm	4390		4240	4880	4070
Oxidation-Reduction Potential, mV E_c	+1		+38	+41	+29
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid	24		24	18	
Carbohydrate, mg/L as glucose	189		113		
Carboxyl, mg/L as acetic acid			BDL	281	
Protein, mg/L as leucine			65	BDL	
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N			90	58	74
Ammonia, mg/L as N			72	43	54
Orthophosphate, mg/L as P			1.1	0.8	1.3
Chlorides, mg/L	547		455	431	439
Sulfides, mg/L					
Total Solids, mg/L	4141		3575	2875	3023
Total Volatile Solids, mg/L	1642		1875	2026	1680
Total Suspended Solids, mg/L	173		170	167	106
Volatile Suspended Solids, mg/L	125		80	24	30
Total Dissolved Solids, mg/L	3968		3405	2708	2917
Volatile Dissolved Solids, mg/L	1517		1795	2002	1650
Cadmium, mg/L	0.3		0.3	0.2	0.1
Calcium, mg/L	600		563	525	555
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	68		15	30	45
Manganese, mg/L	2.4		1.7	1.4	2.0
Magnesium, mg/L	111		90	75	95
Nickel, mg/L	0.43		0.35	0.25	1.0
Sodium, mg/L	585		465	450	465
Potassium, mg/L	540		458	428	443
Zinc, mg/L	90		55	60	68

TABLE 15 (continued)

Time Since Loading, day	553	560	571	575	582
Chemical Oxygen Demand, mg/L	1760	2063	2839	3354	3704
Biochemical Oxygen Demand (BOD_5), mg/L	905	1080	1500	1700	1867
pH	7.50	6.79	5.82	6.68	6.58
Alkalinity, mg/L as $CaCO_3$	3049		863	1377	1416
Conductivity, µmho/cm	4240	3990	4470	4110	4540
Oxidation-Reduction Potential, mV E_c	+10	-18	-87	-112	-54
Acetic Acid, mg/L			507	585	
Propionic Acid, mg/L			450	488	
Isobutyric Acid, mg/L			33	31	
Butyric Acid, mg/L			68	79	
Total Volatile Acids, mg/L as acetic acid			940	1056	
Aromatic Hydroxyl, mg/L as tannic acid		21	35	36	50
Carbohydrate, mg/L as glucose	141	144	208	225	250
Carboxyl, mg/L as acetic acid		75	388	1309	1300
Protein, mg/L as leucine	263				
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		45	66	64	
Ammonia, mg/L as N	63	45	49	54	66
Orthophosphate, mg/L as P	0.7	1.4	2.1	0.5	0.4
Chlorides, mg/L	439	425	415	439	463
Sulfides, mg/L					
Total Solids, mg/L	3248	3458	3883	4025	4207
Total Volatile Solids, mg/L	1014	1206	1571	1638	1714
Total Suspended Solids, mg/L	66	144	184	136	248
Volatile Suspended Solids, mg/L	24	92	129	102	153
Total Dissolved Solids, mg/L	3182	3314	3699	3889	3959
Volatile Dissolved Solids, mg/L	990	1114	1442	1536	1561
Cadmium, mg/L	0.3	0.3	0.5	0.5	0.55
Calcium, mg/L	630	655	675	825	838
Chromium, mg/L					
C pper, mg/L					
Iron, mg/L	45	35	55	60	85
Manganese, mg/L	2.2	2.1	2.5	2.4	2.4
Magnesium, mg/L	100	100	63	6	63
Nickel, mg/L	0.50	0.40	0.50	0.60	0.60
Sodium, mg/L	480	480	300	338	356
Potassium, mg/L	435	488	375	313	363
Zinc, mg/L	75	90	92	98	106

TABLE 15 (continued)

Time Since Loading, day	589	596	603	610	617
Chemical Oxygen Demand, mg/L	3790	4469	4704	4582	5106
Biochemical Oxygen Demand (BOD_5), mg/L	1970	2250	2400	2300	2500
pH	6.27	6.29	6.06	6.02	5.97
Alkalinity, mg/L as $CaCO_3$	1442	1598	1667	1727	1755
Conductivity, µmho/cm	4020	4180	4220	4400	4720
Oxidation-Reduction Potential, mV E_c	-120	-11	-34	-43	-61
Acetic Acid, mg/L	697	1027			1269
Propionic Acid, mg/L	493	665			705
Isobutyric Acid, mg/L	49	35			124
Butyric Acid, mg/L	121	136			253
Total Volatile Acids, mg/L as acetic acid	1213	1683			2098
Aromatic Hydroxyl, mg/L as tannic acid	33	49	65	65	105
Carbohydrate, mg/L as glucose	253	214	212	420	
Carboxyl, mg/L as acetic acid	1541	4368	4973	5468	6505
Protein, mg/L as leucine					
Total Carbon, mg/L	1150	1800	1900	1938	2075
Total Organic Carbon, mg/L		1798	1900	1935	2074
Total Inorganic Carbon, mg/L		2	BDL	3	1
Total Kjeldahl Nitrogen, mg/L as N	81	61	68	68	74
Ammonia, mg/L as N	77	74	58	59	53
Orthophosphate, mg/L as P	1.1	1.6	2.3	3.4	3.8
Chlorides, mg/L	478	484	475	487	474
Sulfides, mg/L					
Total Solids, mg/L	4505	4962			
Total Volatile Solids, mg/L	1921	2229			
Total Suspended Solids, mg/L	166	192			
Volatile Suspended Solids, mg/L	127	113			
Total Dissolved Solids, mg/L	4339	4770			
Volatile Dissolved Solids, mg/L	1794	2116			
Cadmium, mg/L	0.5	0.5	0.43	0.34	0.42
Calcium, mg/L	796	625	712	750	812
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	91	100	115	120	120
Manganese, mg/L	2.5	2.8	3.1	2.8	2.5
Magnesium, mg/L	78	78	95	81	88
Nickel, mg/L	0.60	0.70	0.90	0.80	1.0
Sodium, mg/L	425	425	485	400	469
Potassium, mg/L	363	363	375	375	394
Zinc, mg/L	110	116	120	130	135

TABLE 15 (continued)

Time Since Loading, day	624	631	641	650	655
Chemical Oxygen Demand, mg/L	5125	5818	6100	6315	6163
Biochemical Oxygen Demand (BOD_5), mg/L	2550	2900	3000	3200	3200
pH	5.85	5.76	5.97	6.17	6.14
Alkalinity, mg/L as $CaCO_3$	1768	1788	1832	1967	2047
Conductivity, µmho/cm	4560	4890	4910	4970	5070
Oxidation-Reduction Potential, mV E_c	-59	-39	-55	-75	-72
Acetic Acid, mg/L	1376	1706	1800		
Propionic Acid, mg/L	695	1070	1200		
Isobutyric Acid, mg/L	94	88	100		
Butyric Acid, mg/L	207	357	430		
Total Volatile Acids, mg/L as acetic acid	2145	2877	3134		
Aromatic Hydroxyl, mg/L as tannic acid	104	96			
Carbohydrate, mg/L as glucose	432	267		248	247
Carboxyl, mg/L as acetic acid	8828	7733	7306	7733	7394
Protein, mg/L as leucine	99	107	160		
Total Carbon, mg/L	1925	2175	2250		2262
Total Organic Carbon, mg/L	1925	2175	2250		2231
Total Inorganic Carbon, mg/L	BDL	BDL	BDL		31
Total Kjeldahl Nitrogen, mg/L as N	74	74	101	114	117
Ammonia, mg/L as N	49	61	75	89	84
Orthophosphate, mg/L as P	3.8	3.9	5.8	7.7	6.9
Chlorides, mg/L	480	493	469	494	507
Sulfides, mg/L					
Total Solids, mg/L				5914	5984
Total Volatile Solids, mg/L				2744	2907
Total Suspended Solids, mg/L				145	166
Volatile Suspended Solids, mg/L				74	71
Total Dissolved Solids, mg/L				5769	5818
Volatile Dissolved Solids, mg/L				2670	2836
Cadmium, mg/L	0.43	0.53	0.65	0.46	0.46
Calcium, mg/L	875	981	667	825	938
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	129	140	146	150	150
Manganese, mg/L	4.0	4.0	4.0	4.0	4.5
Magnesium, mg/L	75	125	78	93	96
Nickel, mg/L	1.0	1.0	1.0	1.0	1.05
Sodium, mg/L	535	550	435	444	469
Potassium, mg/L	406	450	406	406	463
Zinc, mg/L	148	150	154	156	188

TABLE 15 (continued)

Time Since Loading, day	662	669	676	683	686
Chemical Oxygen Demand, mg/L	5579	5382			4090
Biochemical Oxygen Demand (BOD_5), mg/L		2700			2300
pH	6.21	6.08			5.80
Alkalinity, mg/L as $CaCO_3$	1768	1732			1375
Conductivity, µmho/cm	5600	5300			4500
Oxidation-Reduction Potential, mV E_c	-76	-65			-47
Acetic Acid, mg/L	1292	1059			584
Propionic Acid, mg/L	1303	1123			942
Isobutyric Acid, mg/L	176	109			65
Butyric Acid, mg/L	416	344			201
Total Volatile Acids, mg/L as acetic acid	2752	2278			1529
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	5233	5122			5083
Protein, mg/L as leucine		244			
Total Carbon, mg/L	2150	2050			
Total Organic Carbon, mg/L	2118	2008			
Total Inorganic Carbon, mg/L	32	42			
Total Kjeldahl Nitrogen, mg/L as N	103	97			92
Ammonia, mg/L as N	77			56	
Orthophosphate, mg/L as P	15.0	0.9			3.6
Chlorides, mg/L	427	436		383	
Sulfides, mg/L					
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	0.3	0.38			0.29
Calcium, mg/L	625	925			
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	150	105			138
Manganese, mg/L	3.3	4.0			
Magnesium, mg/L	80	118			
Nickel, mg/L	1.0	1.06			0.75
Sodium, mg/L	550	688			
Potassium, mg/L	450	463			
Zinc, mg/L	110	212			98

TABLE 15 (continued)

Time Since Loading, day	690	697	705	711	718
Chemical Oxygen Demand, mg/L	4741	4571	5037	5220	
Biochemical Oxygen Demand (BOD_5), mg/L			2533		
pH	6.53	6.29	6.26	6.46	
Alkalinity, mg/L as $CaCO_3$	1768	1625	1592	1786	
Conductivity, μmho/cm	4700	4500	4800		
Oxidation-Reduction Potential, mV E_c	-52	-52			
Acetic Acid, mg/L	589	435	203	224	
Propionic Acid, mg/L	1076	763	342	433	
Isobutyric Acid, mg/L	43	62	BDL	37	
Butyric Acid, mg/L	194	140	BDL	90	
Total Volatile Acids, mg/L as acetic acid	1623	1191	480	662	
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	4111				
Protein, mg/L as leucine		317			
Total Carbon, mg/L	1675	1725	1575	1712	
Total Organic Carbon, mg/L	1648	1668	1568	1700	
Total Inorganic Carbon, mg/L	27	57	7	12	
Total Kjeldahl Nitrogen, mg/L as N	90	55	80	81	
Ammonia, mg/L as N	66	49	59	59	
Orthophosphate, mg/L as P	1.7	8.2	1.8	2.3	
Chlorides, mg/L	394	405	449	416	
Sulfides, mg/L					
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	0.31	0.25	0.35	0.32	
Calcium, mg/L					
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	147	156	138	138	
Manganese, mg/L					
Magnesium, mg/L					
Nickel, mg/L	0.75	0.75	0.65	0.56	
Sodium, mg/L					
Potassium, mg/L					
Zinc, mg/L	78	98	78		

TABLE 16. LEACHATE ANALYSIS FROM COLUMN 4

Time Since Loading, day	35	47	72	86	93
Chemical Oxygen Demand, mg/L	13800	13830	11790	11300	10560
Biochemical Oxygen Demand (BOD_5), mg/L	6700	6100			8200
pH	5.50	5.96	6.01		6.17
Alkalinity, mg/L as $CaCO_3$	1910		2230		1980
Conductivity, µmho/cm		8200	7400		7200
Oxidation-Reduction Potential, mV E_c				-80	
Acetic Acid, mg/L					519
Propionic Acid, mg/L					454
Isobutyric Acid, mg/L					BDL
Butyric Acid, mg/L					489
Total Volatile Acids, mg/L as acetic acid					1220
Aromatic Hydroxyl, mg/L as tannic acid	99	159	161	88	87
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	112	112	96	86	93
Ammonia, mg/L as N	8	8	7	6	8
Orthophosphate, mg/L as P	0.8	0.8	0.3	BDL	0.1
Chlorides, mg/L			1090	1080	1110
Sulfides, mg/L					0.3
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	10	10	80		
Calcium, mg/L	400	450	470		
Chromium, mg/L	BDL	BDL	BDL		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L	150	130	100		
Manganese, mg/L	9.6	9.0	9.2		
Magnesium, mg/L	300	250	280		
Nickel, mg/L	1.0	1.7	0.9		
Sodium, mg/L	1060	1020	980		
Potassium, mg/L	680	720	640		
Zinc, mg/L	400	500	500		

TABLE 16 (continued)

Time Since Loading, day	102	108	114	128	150
Chemical Oxygen Demand, mg/L			10390	7370	
Biochemical Oxygen Demand (BOD_5), mg/L					
pH		6.43		6.34	
Alkalinity, mg/L as $CaCO_3$		2170	2250	1440	
Conductivity, µmho/cm	7000	6800	7000		
Oxidation-Reduction Potential, mV E_c					
Acetic Acid, mg/L			581		
Propionic Acid, mg/L			477		
Isobutyric Acid, mg/L			BDL		
Butyric Acid, mg/L			563		
Total Volatile Acids, mg/L as acetic acid			1360		
Aromatic Hydroxyl, mg/L as tannic acid	130	79	60	28	
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid					
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	89	93	89	83	
Ammonia, mg/L as N	7	7	8	6	
Orthophosphate, mg/L as P	0.1	0.1	0.2	0.2	
Chlorides, mg/L	1130	1130	1130	975	970
Sulfides, mg/L					
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L	5.0	4.0	3.2	1.8	1.5
Calcium, mg/L	320	300	3205		360
Chromium, mg/L	BDL	BDL	T	T	T
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	82	45	40	25	21
Manganese, mg/L	9.0	8.6	9.3	7.0	7.5
Magnesium, mg/L	260	250	250	100	230
Nickel, mg/L	1.1	1.1	0.88	0.5	0.56
Sodium, mg/L	1040	1000	1100	750	940
Potassium, mg/L	580	520	510	400	430
Zinc, mg/L	350	260	240	130	160

TABLE 16 (continued)

Time Since Loading, day	153	164	179	197	211
Chemical Oxygen Demand, mg/L	8178	8560		2550	2780
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	7.20	6.58	6.55		6.98
Alkalinity, mg/L as $CaCO_3$		2050	1800	1380	1540
Conductivity, µmho/cm			5100	4000	3900
Oxidation-Reduction Potential, mV E_c		-30	-65		-70
Acetic Acid, mg/L		470			400
Propionic Acid, mg/L		210			136
Isobutyric Acid, mg/L		BDL			BDL
Butyric Acid, mg/L		BDL			150
Total Volatile Acids, mg/L as acetic acid		680			650
Aromatic Hydroxyl, mg/L as tannic acid		71	54	37	66
Carbohydrate, mg/L as glucose			349	203	250
Carboxyl, mg/L as acetic acid		1760	1790		450
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N		74	74	51	
Ammonia, mg/L as N		7	6		6
Orthophosphate, mg/L as P		0.7	0.8		0.7
Chlorides, mg/L		965	845	780	790
Sulfides, mg/L					0.03
Total Solids, mg/L					
Total Volatile Solids, mg/L					
Total Suspended Solids, mg/L					
Volatile Suspended Solids, mg/L					
Total Dissolved Solids, mg/L					
Volatile Dissolved Solids, mg/L					
Cadmium, mg/L			1.25		0.5
Calcium, mg/L	200		95		140
Chromium, mg/L			BDL	BDL	BDL
Copper, mg/L			0.2	BDL	BDL
Iron, mg/L			31		21
Manganese, mg/L			6.0		2.4
Magnesium, mg/L			100		210
Nickel, mg/L			0.55		0.4
Sodium, mg/L			590	675	
Potassium, mg/L			310		380
Zinc, mg/L			190	25	

TABLE 16 (continued)

Time Since Loading, day	224	226	233	240	247
Chemical Oxygen Demand, mg/L	2530	2480	3036	3040	2840
Biochemical Oxygen Demand (BOD_5), mg/L					
pH			6.65	6.72	
Alkalinity, mg/L as $CaCO_3$			1500	1610	
Conductivity, μmho/cm	4400	4300		4150	4300
Oxidation-Reduction Potential, mV E_c			-80	-88	
Acetic Acid, mg/L	400				
Propionic Acid, mg/L	80				
Isobutyric Acid, mg/L	20				
Butyric Acid, mg/L	169				
Total Volatile Acids, mg/L as acetic acid	620				
Aromatic Hydroxyl, mg/L as tannic acid	54	68	49	71	88
Carbohydrate, mg/L as glucose	213	191	224	292	
Carboxyl, mg/L as acetic acid		355	495	400	400
Protein, mg/L as leucine					
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	65	75	59	57	50
Ammonia, mg/L as N	5		6	6	6
Orthophosphate, mg/L as P	0.2	0.3	0.3	0.3	0.6
Chlorides, mg/L	770	780	785	800	755
Sulfides, mg/L			0.067	0.70	
Total Solids, mg/L			5640	5600	5380
Total Volatile Solids, mg/L			2320	3100	2610
Total Suspended Solids, mg/L			283	267	203
Volatile Suspended Solids, mg/L			137	117	99
Total Dissolved Solids, mg/L			5357	5333	5177
Volatile Dissolved Solids, mg/L			2183	2983	2511
Cadmium, mg/L		0.50	0.42	0.38	0.45
Calcium, mg/L		200	210	210	210
Chromium, mg/L	BDL	0.2	BDL	0.2	0.2
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L		32	50	45	48
Manganese, mg/L		2.2	2.5	2.2	2.2
Magnesium, mg/L		92	98	90	90
Nickel, mg/L		0.43	0.40	0.35	0.38
Sodium, mg/L		440	280	360	320
Potassium, mg/L		250	480	380	400
Zinc, mg/L			55	36	36

TABLE 16 (continued)

Time Since Loading, day	254	261	268	273	282
Chemical Oxygen Demand, mg/L	2445	2756	3036	3835	4676
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.55	7.21	6.53	6.39	6.35
Alkalinity, mg/L as $CaCO_3$	1360	1560	1410	1220	1460
Conductivity, µmho/cm		3750	4050	4100	4950
Oxidation-Reduction Potential, mV E_c	-58	-90	-152	-69	-250
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid	62	70	14	28	71
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	865	605	605		
Protein, mg/L as leucine					
Total Carbon, mg/L	840	875	860	1240	1705
Total Organic Carbon, mg/L	775	800	800	1160	1625
Total Inorganic Carbon, mg/L	65	75	60	80	80
Total Kjeldahl Nitrogen, mg/L as N	50	46	50	55	54
Ammonia, mg/L as N	6	6	6	6	6
Orthophosphate, mg/L as P	0.7	0.7	0.9	1.2	1.9
Chlorides, mg/L		680	685	685	
Sulfides, mg/L	0.2	0.08	0.21	2.6	0.80
Total Solids, mg/L	5500	5480	5510	5490	5500
Total Volatile Solids, mg/L	2570	2550	2580	2500	2550
Total Suspended Solids, mg/L	185	189	190	200	192
Volatile Suspended Solids, mg/L	98	100	105	101	108
Total Dissolved Solids, mg/L	5215	5281	5320	5290	5308
Volatile Dissolved Solids, mg/L	2472	2450	2475	2399	2442
Cadmium, mg/L	0.34	0.23	0.35		
Calcium, mg/L	220	190	190		
Chromium, mg/L	T	0.1	0.1		
Copper, mg/L	BDL	BDL	BDL		
Iron, mg/L	45	60	65		
Manganese, mg/L	2.0	2.4	3.0		
Magnesium, mg/L	162	162	162		
Nickel, mg/L	0.40	0.3	0.51		
Sodium, mg/L	475	475	475		
Potassium, mg/L	500	450	500		
Zinc, mg/L			30		

TABLE 16 (continued)

Time Since Loading, day	289	298	303	310	318
Chemical Oxygen Demand, mg/L	4856	5382		5178	6782
Biochemical Oxygen Demand (BOD_5), mg/L					
pH	6.25			6.34	
Alkalinity, mg/L as $CaCO_3$	1360	1960		2370	
Conductivity, µmho/cm	5000	5100	5000	5260	5250
Oxidation-Reduction Potential, mV E_c	-133		-250	-40	
Acetic Acid, mg/L	1450			3500	2300
Propionic Acid, mg/L	810			1460	2100
Isobutyric Acid, mg/L	BDL			40	BDL
Butyric Acid, mg/L	BDL			380	380
Total Volatile Acids, mg/L as acetic acid	2100			4800	3200
Aromatic Hydroxyl, mg/L as tannic acid	25	10	71	34	49
Carbohydrate, mg/L as glucose					407
Carboxyl, mg/L as acetic acid	955	3420	5840	2280	7220
Protein, mg/L as leucine					
Total Carbon, mg/L	1845	1925	1940	1490	2000
Total Organic Carbon, mg/L	1775	1875	1850	1400	1920
Total Inorganic Carbon, mg/L	70	50	90	90	80
Total Kjeldahl Nitrogen, mg/L as N	75	55	89	93	100
Ammonia, mg/L as N	5	6		5	5
Orthophosphate, mg/L as P	1.6	2.1	1.9	1.8	2.2
Chlorides, mg/L			680	695	710
Sulfides, mg/L	0.35		0.08		
Total Solids, mg/L	5570	5100	5810	6280	6300
Total Volatile Solids, mg/L	2420	3000	3012	3030	3200
Total Suspended Solids, mg/L	79	95	113	185	190
Volatile Suspended Solids, mg/L	46	67	91	123	130
Total Dissolved Solids, mg/L	5491	5005	5697	6095	6110
Volatile Dissolved Solids, mg/L	2374	2933	2921	2907	3070
Cadmium, mg/L	0.65	0.30	0.33	0.41	0.35
Calcium, mg/L	250	220	210	270	300
Chromium, mg/L	0.1	T	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	70	60	68	78	82
Manganese, mg/L	3.4	3.6	4.0	4.6	4.6
Magnesium, mg/L	140	110	130	120	90
Nickel, mg/L	0.71	0.45	0.50	0.65	0.63
Sodium, mg/L	440	380	320	430	405
Potassium, mg/L	520	520	500		
Zinc, mg/L					

TABLE 16 (continued)

Time Since Loading, day	324	331	338	345	352
Chemical Oxygen Demand, mg/L	7227	5434	6179	7500	10972
Biochemical Oxygen Demand (BOD_5), mg/L	4680	3310	2900	4000	6140
pH	6.05	5.98	5.92	5.69	6.00
Alkalinity, mg/L as $CaCO_3$	2250	2130	2070	1660	2490
Conductivity, μmho/cm	5450	5500	5600		6100
Oxidation-Reduction Potential, mV E_c	-25	-100	-15	-25	-50
Acetic Acid, mg/L	1750	2960	1200	2700	
Propionic Acid, mg/L	350	990	350	920	
Isobutyric Acid, mg/L	BDL	80	50	BDL	
Butyric Acid, mg/L	250	430	80	BDL	
Total Volatile Acids, mg/L as acetic acid	2300	4130	1540	3400	
Aromatic Hydroxyl, mg/L as tannic acid	42	33	42	28	25
Carbohydrate, mg/L as glucose	300				
Carboxyl, mg/L as acetic acid		8180	6915	3520	7240
Protein, mg/L as leucine					
Total Carbon, mg/L	2250	2200	2050	2350	2350
Total Organic Carbon, mg/L	2162	2120	2000	2300	2300
Total Inorganic Carbon, mg/L	90	80	50	50	50
Total Kjeldahl Nitrogen, mg/L as N	107	112	114	115	115
Ammonia, mg/L as N	4	4	5	4	4
Orthophosphate, mg/L as P	2.3	2.4	2.5	2.5	2.5
Chlorides, mg/L	670		740		740
Sulfides, mg/L	1.8			0.021	
Total Solids, mg/L	5100	5250	5275	5260	4800
Total Volatile Solids, mg/L	3000	3100	2600	2447	2210
Total Suspended Solids, mg/L	200	207	176	181	217
Volatile Suspended Solids, mg/L	124	116	121	123	100
Total Dissolved Solids, mg/L	4900	5043	5099	5079	4583
Volatile Dissolved Solids, mg/L	2876	2984	2479	2324	2110
Cadmium, mg/L	0.50	0.40	0.44	0.50	0.44
Calcium, mg/L	270	310			
Chromium, mg/L	BDL	BDL	BDL	BDL	BDL
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Iron, mg/L	88	100	100	130	130
Manganese, mg/L	5.0	7.0	5.0	5.5	5.3
Magnesium, mg/L	110	125	80	80	70
Nickel, mg/L	0.80	0.66	0.83	0.95	0.95
Sodium, mg/L	390	360	360	575	460
Potassium, mg/L	100		620	620	680
Zinc, mg/L	100				140

TABLE 16 (continued)

Time Since Loading, day	359	367	374	381	387
Chemical Oxygen Demand, mg/L	7459	6810	7100	5714	5315
Biochemical Oxygen Demand (BOD_5), mg/L	3580	3400	3760	2690	2500
pH	5.84		6.44	6.15	
Alkalinity, mg/L as $CaCO_3$	2130		2250		
Conductivity, µmho/cm	6200		5550	5650	5500
Oxidation-Reduction Potential, mV E_c			-220	-40	
Acetic Acid, mg/L			1450		
Propionic Acid, mg/L			380		
Isobutyric Acid, mg/L			BDL		
Butyric Acid, mg/L			300		
Total Volatile Acids, mg/L as acetic acid			2000		
Aromatic Hydroxyl, mg/L as tannic acid	26		17	17	58
Carbohydrate, mg/L as glucose				186	428
Carboxyl, mg/L as acetic acid	5190		7585		7110
Protein, mg/L as leucine					
Total Carbon, mg/L	2450	1900	2000	2000	1850
Total Organic Carbon, mg/L	2375	1780	1900	1920	1700
Total Inorganic Carbon, mg/L	80	125	100	80	150
Total Kjeldahl Nitrogen, mg/L as N	114	117	116	120	118
Ammonia, mg/L as N	4	4	5	5	5
Orthophosphate, mg/L as P	2.6	2.6	2.6	2.7	2.6
Chlorides, mg/L	770		784	795	765
Sulfides, mg/L			0.027		
Total Solids, mg/L	5400	5310	4560	4303	4050
Total Volatile Solids, mg/L	2200	2225	1925	1906	1845
Total Suspended Solids, mg/L	159	166	173	149	167
Volatile Suspended Solids, mg/L	101	106	110	97	83
Total Dissolved Solids, mg/L	5241	5144	4387	4154	3883
Volatile Dissolved Solids, mg/L	2099	2119	1815	1809	1762
Cadmium, mg/L	0.41		0.20	0.28	
Calcium, mg/L					
Chromium, mg/L	BDL		BDL	BDL	
Copper, mg/L	BDL		BDL	BDL	
Iron, mg/L	120			85	
Manganese, mg/L	4.3		2.4	3.8	
Magnesium, mg/L	50			50	
Nickel, mg/L	0.73		0.44	1.18	
Sodium, mg/L	250			375	
Potassium, mg/L	700		690	700	
Zinc, mg/L			115		130

TABLE 16 (continued)

Time Since Loading, day	483	490	529	539	546
Chemical Oxygen Demand, mg/L	5188	2870	933	951	1107
Biochemical Oxygen Demand (BOD_5), mg/L	2700	1500	410	480	600
pH	6.62	6.56	6.81	6.72	6.84
Alkalinity, mg/L as $CaCO_3$	2682	2538	1111	924	5830
Conductivity, μmho/cm	5290	5170	4170	4100	4140
Oxidation-Reduction Potential, mV E_c	+75	+142	-8	-15	-30
Acetic Acid, mg/L					
Propionic Acid, mg/L					
Isobutyric Acid, mg/L					
Butyric Acid, mg/L					
Total Volatile Acids, mg/L as acetic acid					
Aromatic Hydroxyl, mg/L as tannic acid	24	34	15	17	20
Carbohydrate, mg/L as glucose	193	174	118		147
Carboxyl, mg/L as acetic acid		2394	BDL		75
Protein, mg/L as leucine		100	120		
Total Carbon, mg/L					
Total Organic Carbon, mg/L					
Total Inorganic Carbon, mg/L					
Total Kjeldahl Nitrogen, mg/L as N	37	26	30	32	35
Ammonia, mg/L as N	64	68	20	16	25
Orthophosphate, mg/L as P	0.8	0.3	0.3	0.6	0.6
Chlorides, mg/L	668	692	574	615	615
Sulfides, mg/L					
Total Solids, mg/L	4912	4781	3560	2968	3000
Total Volatile Solids, mg/L	1911	1824	2115	2203	1110
Total Suspended Solids, mg/L	144	132	116	94	78
Volatile Suspended Solids, mg/L	78	88	66	9	12
Total Dissolved Solids, mg/L	4768	4649	3444	2874	2922
Volatile Dissolved Solids, mg/L	1833	1736	2049	2194	1098
Cadmium, mg/L	0.1	0.1	0.1	0.1	0.1
Calcium, mg/L	825	795	510	600	630
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	45		30	45	45
Manganese, mg/L	3.2	3.0	2.0	2.0	2.1
Magnesium, mg/L	155	130	102	75	95
Nickel, mg/L	0.50	0.48	0.38	0.43	0.58
Sodium, mg/L	1050	1650	615	540	570
Potassium, mg/L	488	428	435	345	345
Zinc, mg/L	98	105	45	45	45

TABLE 16 (continued)

Time Since Loading, day	553	560	571	575	582
Chemical Oxygen Demand, mg/L	1284	1460	1461	2563	2881
Biochemical Oxygen Demand (BOD_5), mg/L	707	780	746	1467	
pH	7.15	6.90	5.79	6.69	6.49
Alkalinity, mg/L as $CaCO_3$	5308	5665	791	1142	1197
Conductivity, µmho/cm	4460	4180	4150	4190	4760
Oxidation-Reduction Potential, mV E_c	-25	-58	-115	-138	-38
Acetic Acid, mg/L			491	502	
Propionic Acid, mg/L			380	361	
Isobutyric Acid, mg/L			20	85	
Butyric Acid, mg/L			42	59	
Total Volatile Acids, mg/L as acetic acid			841	893	
Aromatic Hydroxyl, mg/L as tannic acid		28	33		
Carbohydrate, mg/L as glucose	237	160	163	195	158
Carboxyl, mg/L as acetic acid	25	BDL	213	886	1423
Protein, mg/L as leucine	190			117	
Total Carbon, mg/L					1050
Total Organic Carbon, mg/L					1023
Total Inorganic Carbon, mg/L					27
Total Kjeldahl Nitrogen, mg/L as N	31	27	26	24	35
Ammonia, mg/L as N	29	20	20	24	24
Orthophosphate, mg/L as P	3.7	2.7	3.1	0.3	0.3
Chlorides, mg/L	590	620	572	602	609
Sulfides, mg/L					
Total Solids, mg/L	3180	3362	3544	3707	3987
Total Volatile Solids, mg/L	826	956	1116	1273	1404
Total Suspended Solids, mg/L	44	104	145	104	146
Volatile Suspended Solids, mg/L	16	78	94	70	90
Total Dissolved Solids, mg/L	3136	3258	3399	3603	3841
Volatile Dissolved Solids, mg/L	810	878	1022	1203	1314
Cadmium, mg/L	0.1	0.1	0.2	0.2	0.2
Calcium, mg/L	660	765	788	863	750
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	30	35	50	57	70
Manganese, mg/L	2.1	1.9	2.3	2.2	2.4
Magnesium, mg/L	95	75	60	61	70
Nickel, mg/L	0.50	0.30	0.60	0.40	0.50
Sodium, mg/L	540	525	319	444	456
Potassium, mg/L	375	375	300	260	313
Zinc, mg/L	55	83	90	110	116

TABLE 16 (continued)

Time Since Loading, day	589	596	603	610	617
Chemical Oxygen Demand, mg/L	3548	4115	4267	3700	4426
Biochemical Oxygen Demand (BOD_5), mg/L	1800	2050	2200	2100	2250
pH	6.62	6.15	5.90	5.99	5.95
Alkalinity, mg/L as $CaCO_3$	1225	1392	1511	1537	1457
Conductivity, µmho/cm	3780	4400	4630	4310	4620
Oxidation-Reduction Potential, mV E_c	-84	+7	-12	-40	-49
Acetic Acid, mg/L	670				1375
Propionic Acid, mg/L	418				644
Isobutyric Acid, mg/L	BDL				100
Butyric Acid, mg/L	123				195
Total Volatile Acids, mg/L as acetic acid	1093				2098
Aromatic Hydroxyl, mg/L as tannic acid	35	72	83	73	94
Carbohydrate, mg/L as glucose	172	164	172	162	288
Carboxyl, mg/L as acetic acid	2155	3845	4618	4841	6067
Protein, mg/L as leucine		270			
Total Carbon, mg/L	975	1525	1675	1725	1650
Total Organic Carbon, mg/L		1520	1672	1724	1650
Total Inorganic Carbon, mg/L		5	3	1	BDL
Total Kjeldahl Nitrogen, mg/L as N	24	24	26	25	
Ammonia, mg/L as N	24	20	18	15	14
Orthophosphate, mg/L as P	0.6	0.9	0.9	0.9	1.8
Chlorides, mg/L	660	666	644	613	618
Sulfides, mg/L					
Total Solids, mg/L	4258	4739			
Total Volatile Solids, mg/L	1617	1904			
Total Suspended Solids, mg/L	149	173			
Volatile Suspended Solids, mg/L	103	103			
Total Dissolved Solids, mg/L	4109	4566			
Volatile Dissolved Solids, mg/L	1514	1801			
Cadmium, mg/L	0.2	0.26	0.33	0.25	0.34
Calcium, mg/L	775	812	800	819	881
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	77	89	108	110	115
Manganese, mg/L	2.8	3.1	3.4	2.3	2.5
Magnesium, mg/L	68	95	78	78	88
Nickel, mg/L	0.80	0.85	1.10	1.0	0.95
Sodium, mg/L	500	550	500	563	535
Potassium, mg/L	325	313	300	300	325
Zinc, mg/L	118	122	140	146	150

TABLE 16 (continued)

Time Since Loading, day	624	631	641	650	655
Chemical Oxygen Demand, mg/L	4042	4582	4726	4585	4688
Biochemical Oxygen Demand (BOD_5), mg/L	2050	2300	2400	2300	
pH	5.90	5.86	5.99	6.10	6.13
Alkalinity, mg/L as $CaCO_3$	1504	1552	1564	1634	1701
Conductivity, μmho/cm	4640	4970	4580	4840	4960
Oxidation-Reduction Potential, mV E_c	-55	-31	-52	-57	-59
Acetic Acid, mg/L	974	1776	2039		
Propionic Acid, mg/L	394	834	981		
Isobutyric Acid, mg/L	111	16	40		
Butyric Acid, mg/L	143	164	223		
Total Volatile Acids, mg/L as acetic acid	1467	2575	3014		
Aromatic Hydroxyl, mg/L as tannic acid	93	100	109		
Carbohydrate, mg/L as glucose	344	174		152	175
Carboxyl, mg/L as acetic acid	6829	6217	6150	6828	4544
Protein, mg/L as leucine	87	87	72		
Total Carbon, mg/L	1738	1850	1712		1762
Total Organic Carbon, mg/L	1728	1850	1710		1737
Total Inorganic Carbon, mg/L	10	0	2		25
Total Kjeldahl Nitrogen, mg/L as N		27	26	27	41
Ammonia, mg/L as N		17	18	25	25
Orthophosphate, mg/L as P	2.4	2.2	1.3	1.5	1.7
Chlorides, mg/L	593	580	532	580	567
Sulfides, mg/L					
Total Solids, mg/L				5378	5458
Total Volatile Solids, mg/L				2215	2365
Total Suspended Solids, mg/L				125	88
Volatile Suspended Solids, mg/L				68	65
Total Dissolved Solids, mg/L				5253	5370
Volatile Dissolved Solids, mg/L				2147	2300
Cadmium, mg/L	0.37	0.40	0.43	0.39	0.39
Calcium, mg/L	919	1000	719	800	788
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	123	120	115	113	125
Manganese, mg/L	45.	4.5	5.0	4.5	5.0
Magnesium, mg/L	81	92	70	75	83
Nickel, mg/L	1.10	1.20	1.10	1.10	1.10
Sodium, mg/L	594	535	519	510	535
Potassium, mg/L	269	300	300	313	300
Zinc, mg/L	158	162	160	163	156

TABLE 16 (continued)

Time Since Loading, day	662	669	679	683	686
Chemical Oxygen Demand, mg/L	4264	4563	4980	4800	3420
Biochemical Oxygen Demand (BOD_5), mg/L		2300	2500	2500	
pH	6.26	6.13	6.08	6.21	5.81
Alkalinity, mg/L as $CaCO_3$	1554	1599	1534	1743	1252
Conductivity, µmho/cm	5400	5600	5500	5700	4900
Oxidation-Reduction Potential, mV E_c	-61	-74	-52	-54	-48
Acetic Acid, mg/L	1515	1280	1031	1060	842
Propionic Acid, mg/L	1008	980	841	916	847
Isobutyric Acid, mg/L	48	BDL	BDL	68	97
Butyric Acid, mg/L	250	263	226	189	177
Total Volatile Acids, mg/L as acetic acid	2535	2254	1867	1979	1716
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	5567	5333	5989		4661
Protein, mg/L as leucine		231	258		
Total Carbon, mg/L	1550	1875	1588	1725	
Total Organic Carbon, mg/L	1533	1839	1555	1694	
Total Inorganic Carbon, mg/L	17	36	33	31	
Total Kjeldahl Nitrogen, mg/L as N	43	42	48	48	40
Ammonia, mg/L as N	26		47	30	28
Orthophosphate, mg/L as P	1.7	0.6	2.3	3.3	7.2
Chlorides, mg/L	523	545	577	567	447
Sulfides, mg/L					
Total Solids, mg/L			5374	5319	
Total Volatile Solids, mg/L			2297	2318	
Total Suspended Solids, mg/L			350	138	
Volatile Suspended Solids, mg/L			247	86	
Total Dissolved Solids, mg/L			5024	5381	
Volatile Dissolved Solids, mg/L			2050	2232	
Cadmium, mg/L	0.38	0.38	0.38	0.38	0.30
Calcium, mg/L	1000	300	325	75	
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	105	88	150	150	135
Manganese, mg/L	3.8	4.0	4.0	4.0	
Magnesium, mg/L	90	63	40	15	
Nickel, mg/L	1.1	1.15	1.15	1.06	1.0
Sodium, mg/L	563	563	650	700	
Potassium, mg/L	388	375	425	413	
Zinc, mg/L	170	116	145	148	120

TABLE 16 (continued)

Time Since Loading, day	690	697	705	711	718
Chemical Oxygen Demand, mg/L	4262	4291	2106	4853	4854
Biochemical Oxygen Demand (BOD_5), mg/L		2150	1030		
pH	6.43	6.58	6.30	6.11	
Alkalinity, mg/L as $CaCO_3$	1804	1863	1942	1786	
Conductivity, μmho/cm	5100	5100	5300	5900	
Oxidation-Reduction Potential, mV E_c	-65	-50	-25	-49	
Acetic Acid, mg/L	1032	392	329	847	791
Propionic Acid, mg/L	1025	72	327	1044	1206
Isobutyric Acid, mg/L	33	BDL	BDL	75	62
Butyric Acid, mg/L	170	BDL	BDL	186	184
Total Volatile Acids, mg/L as acetic acid	2001	694	594	1871	1937
Aromatic Hydroxyl, mg/L as tannic acid					
Carbohydrate, mg/L as glucose					
Carboxyl, mg/L as acetic acid	4406				
Protein, mg/L as leucine					
Total Carbon, mg/L	1525	1475	1450	1575	
Total Organic Carbon, mg/L	1496	1415	1425	1552	
Total Inorganic Carbon, mg/L	29	60	15	23	
Total Kjeldahl Nitrogen, mg/L as N	49	48	49	46	37.8
Ammonia, mg/L as N	31	54	29	26	28.0
Orthophosphate, mg/L as P	2.4	2.7	2.6	0.9	1.0
Chlorides, mg/L	480	534	523	558	
Sulfides, mg/L					
Total Solids, mg/L				5234	
Total Volatile Solids, mg/L				2760	
Total Suspended Solids, mg/L				138	
Volatile Suspended Solids, mg/L				104	
Total Dissolved Solids, mg/L				5096	
Volatile Dissolved Solids, mg/L				2232	
Cadmium, mg/L	0.34	0.35	0.40	0.44	
Calcium, mg/L					
Chromium, mg/L					
Copper, mg/L					
Iron, mg/L	135	88	81	119	
Manganese, mg/L					
Magnesium, mg/L					
Nickel, mg/L	0.75	0.88	0.69	0.62	
Sodium, mg/L					
Potassium, mg/L					
Zinc, mg/L	88	80	82		75

of leachate, it was necessary to take into account the withdrawal of chloride by sampling and the addition of chloride on those occasions when tap water was added to the columns to supplement natural rainfall. As a result, leachate volumes were computed by:

$$V_t = \frac{Cl_o V_o - \sum_{t=1}^{n} Cl_s V_s + \sum_{t=1}^{n} Cl_a V_a}{Cl_t} \qquad \ldots(1)$$

where; (Cl_o), (Cl_s), (Cl_a) = concentrations of chloride at time zero, in leachate samples and in added tap water, respectively.

V_o, V_s, V_a = the initial leachate volume, volume of sample and volume of added tap water, respectively.

V_t = the leachate volume at time = t.

Using this equation, it was possible to develope a series of leachate volume factors which, when multiplied by corresponding solute concentrations, yielded an estimate of the total solute masses. (See Appendix Table A-5 for sample calculation.)

As a test of the validity of this technique, it was applied with sodium, another abundant conservative leachate constituant. Resultant plots of sodium mass as a function of time are presented in Figures 13 through 16. Although scatter in the sodium mass data was evident (a reflection of the inherent sensitivity of atomic absorption analysis of this element), little divergence in overall trends in the total masses of sodium was observed in any of the columns. Based on these results, it was concluded that the estimated leachate volumes developed by use of Equation 1 could be used with sufficient confidence for computation of other solute masses.

In the succeeding sections of this report, both mass and concentration data will be presented even though major trends observed in all cases were essentially identical for both. Therefore, in the ensuing data presentation and discussion, analyses will be presented in terms of parameter levels, a term intended to encompass both measures of solute quantity.

General Chronology of Column Operational Characteristics

As indicated previously, the operating history of the simulated landfill columns included an extended drought period during the second year which caused a prolonged cessation of leachate production and tended to influence the observed progress of landfill stabilization into corresponding phases. This sequential process was reflected in the temporal behavior of virtually all leachate parameters. While the chronological details of these phases varied somewhat depending on the specific parameter being examined, a general division of these phases by operational characteristics is presented in Table 17 and was used as a guide to facilitate comparison and evaluation among the various parameters reflecting leachate composition.

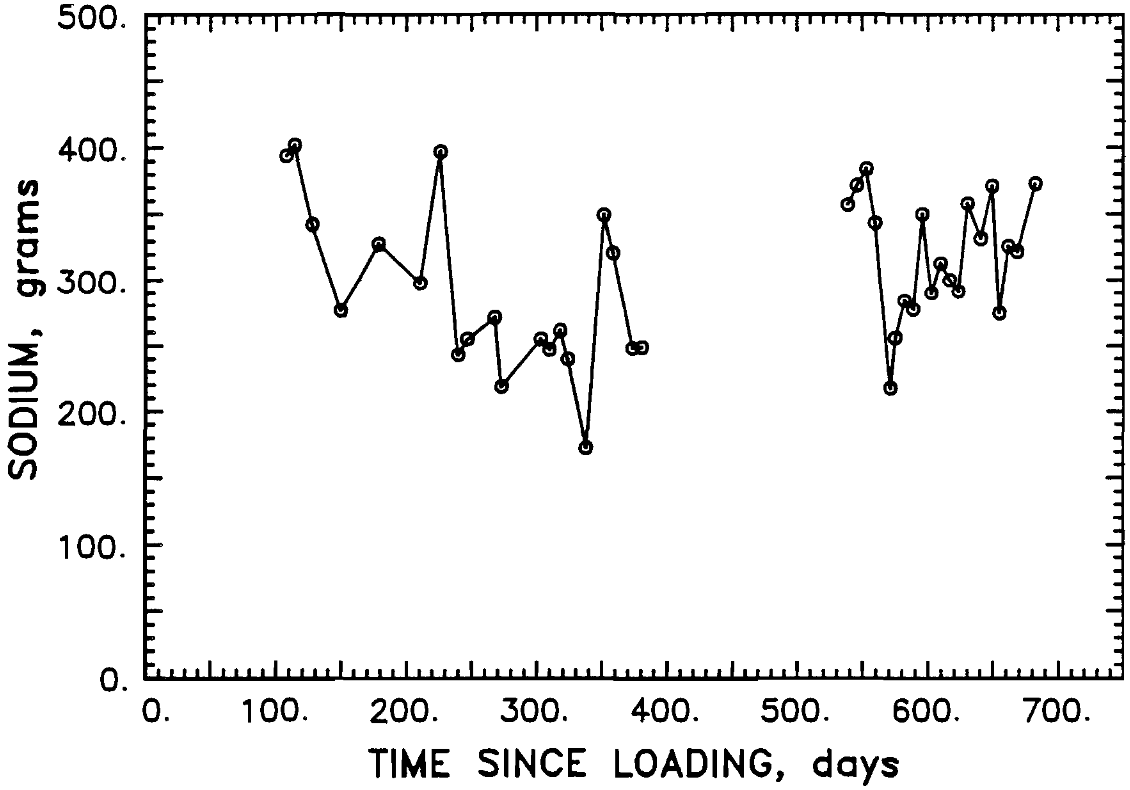


Figure 13. Mass of Sodium in Column 1 Leachate

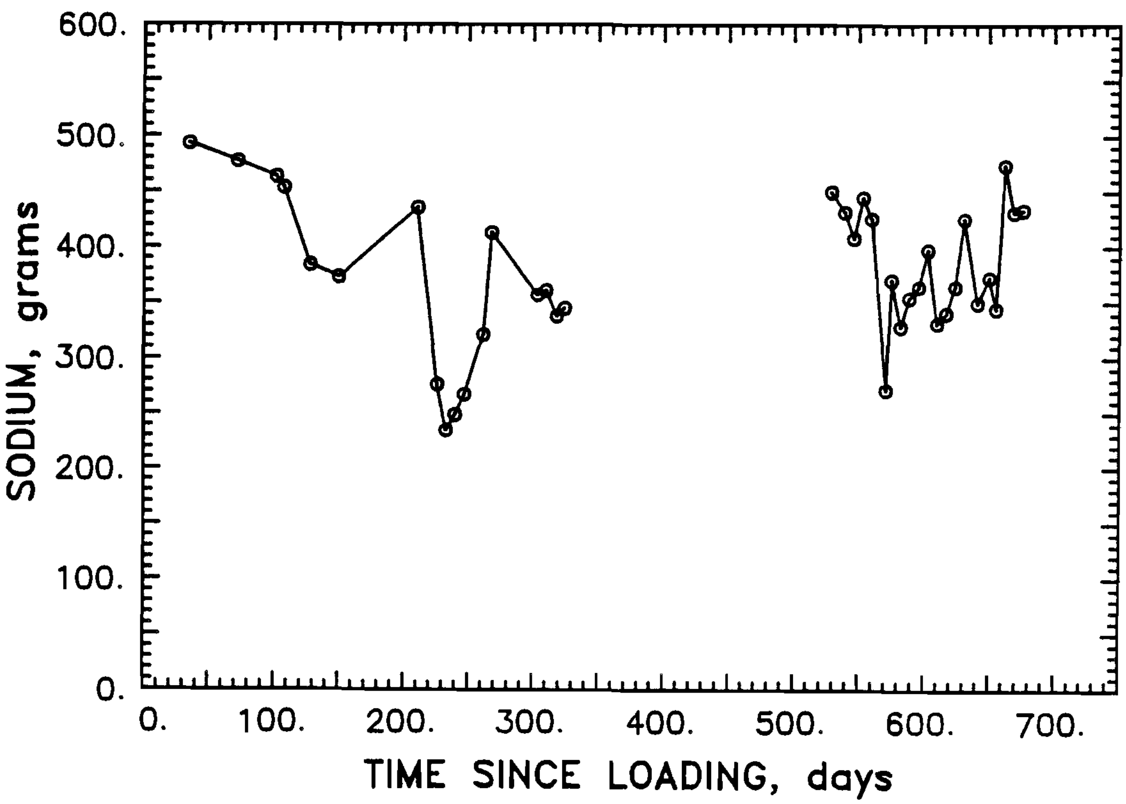


Figure 14. Mass of Sodium in Column 2 Leachate

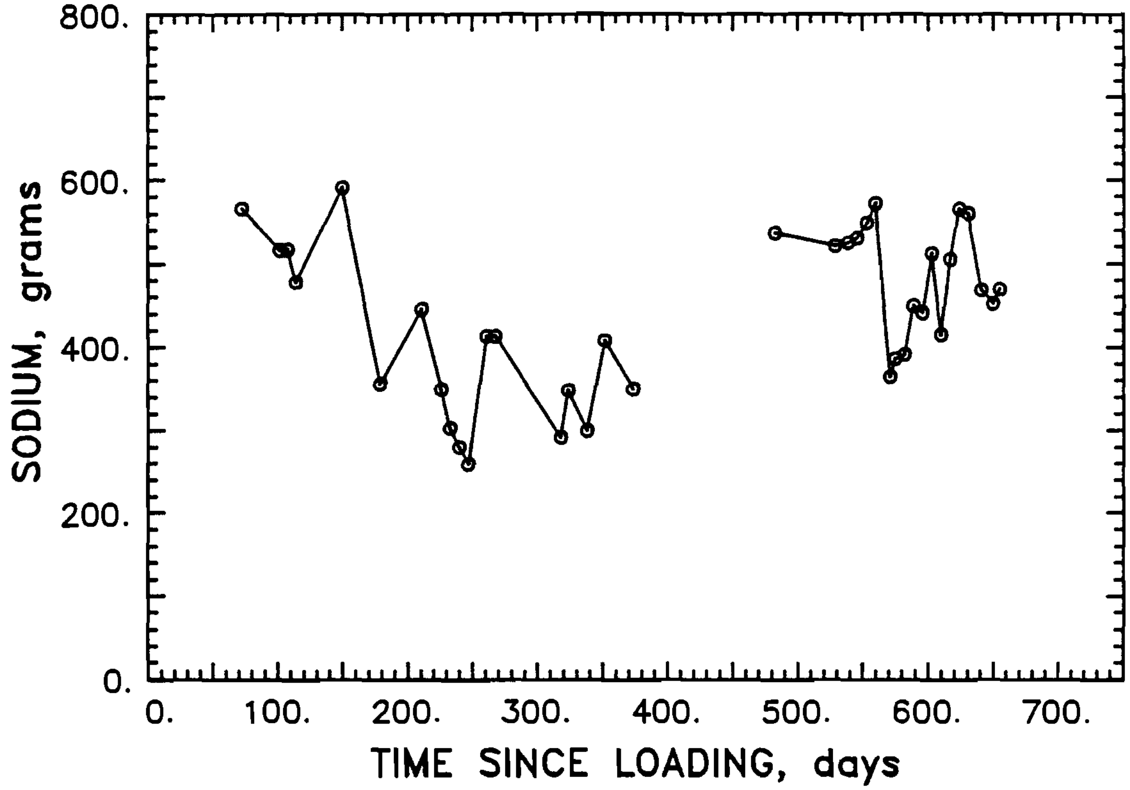


Figure 15. Mass of Sodium in Column 3 Leachate

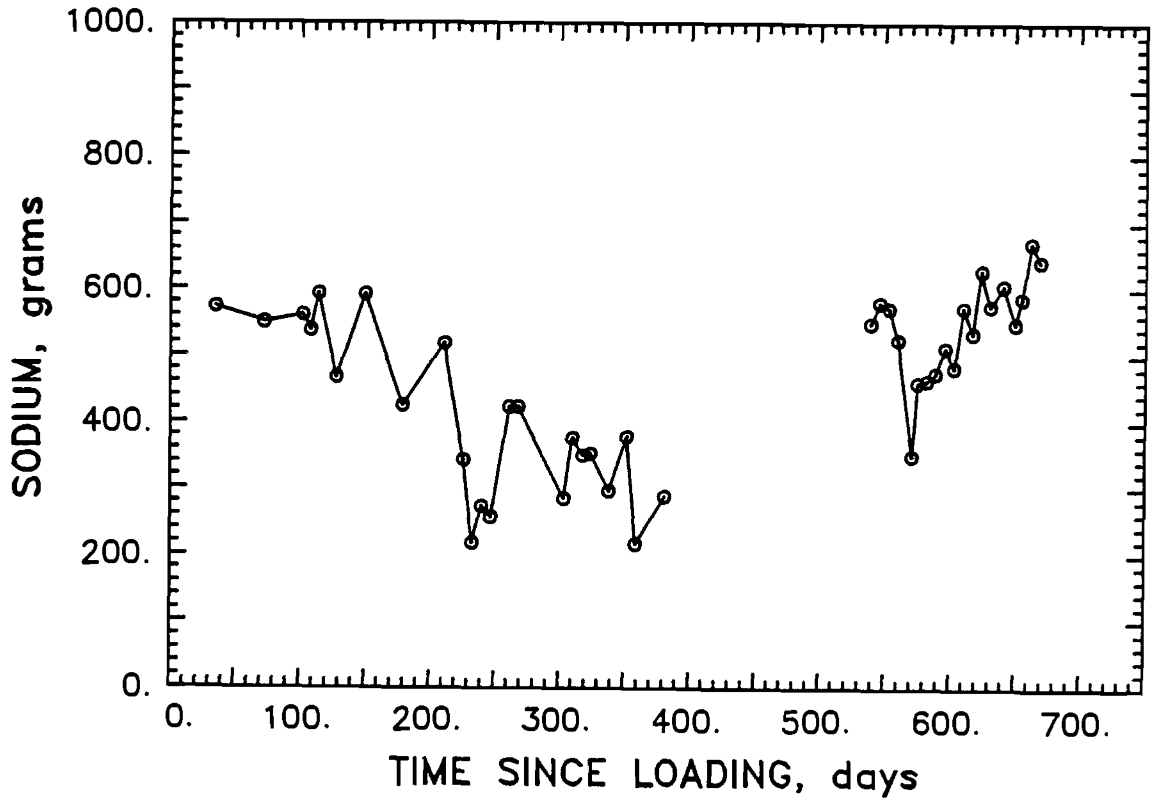


Figure 16. Mass of Sodium in Column 4 Leachate

TABLE 17. PHASES OF SIMULATED LANDFILL OPERATIONS

Experimental Phase	Days	Operational Characteristics
A	0-200	Washout and/or facile production of leachate
B	200-380	Initial micorbially mediated stabilization
B'	380-480	No leachate production or recycle; period of drought
C	480-600	Post-drought resumption of leachate production
D	600-720	Terminal phase of leachate production

Impact of Codisposed Heavy Metal Sludges On Column Behavior

A primary objective of the research reported herein was to obtain data revealing the impact of the heavy metal sludges codisposed with the refuse on the evolution and behavior of the landfill columns. In particular, it was desired to ascertain the maximum level of sludge which the columns could accommodate without detrimental impact on the normal progression of waste stabilization. In addition, valuable information regarding the manner in which heavy metal toxicity would be manifested in the landfill columns was to be gathered and systematized.

Changes in Heavy Metals with Time--

The behavior of toxic heavy metals in the leachates received major focus in these evaluations. Shown in Figures 17 through 27 are the variations in the leachate concentrations and masses of zinc, cadmium and nickel during the project period. Cadmium concentrations in the leachate from Column 1 were consistantly at or near the lowest detectable level and, therefore, were not plotted. The gaps in the plotted data represent the period of zero leachate production corresponding to the drought period previously identified.

Fluctuations of the three metals were essentially similar, although the concentration levels differed dramatically. There was an initial washout and fixation of readily soluble metals from the sludges, followed by a period of stability leading up to the cessation of leachate production around Day 380. This stable concentration was maintained for a considerable period immediately following the resumption of leachate production, but a discernable trend toward increasing metal levels was observed for most of the metals toward the termination of the studies.

Mobilization of Heavy Metals During Operational Phases--

Average levels of heavy metals in the four operational phases outlined above are shown in bar graph form in Figures 28 through 30. The trends observed from the concentration and mass versus time plots are again evident. An initially rapid washout of readily mobilized metals was followed by a

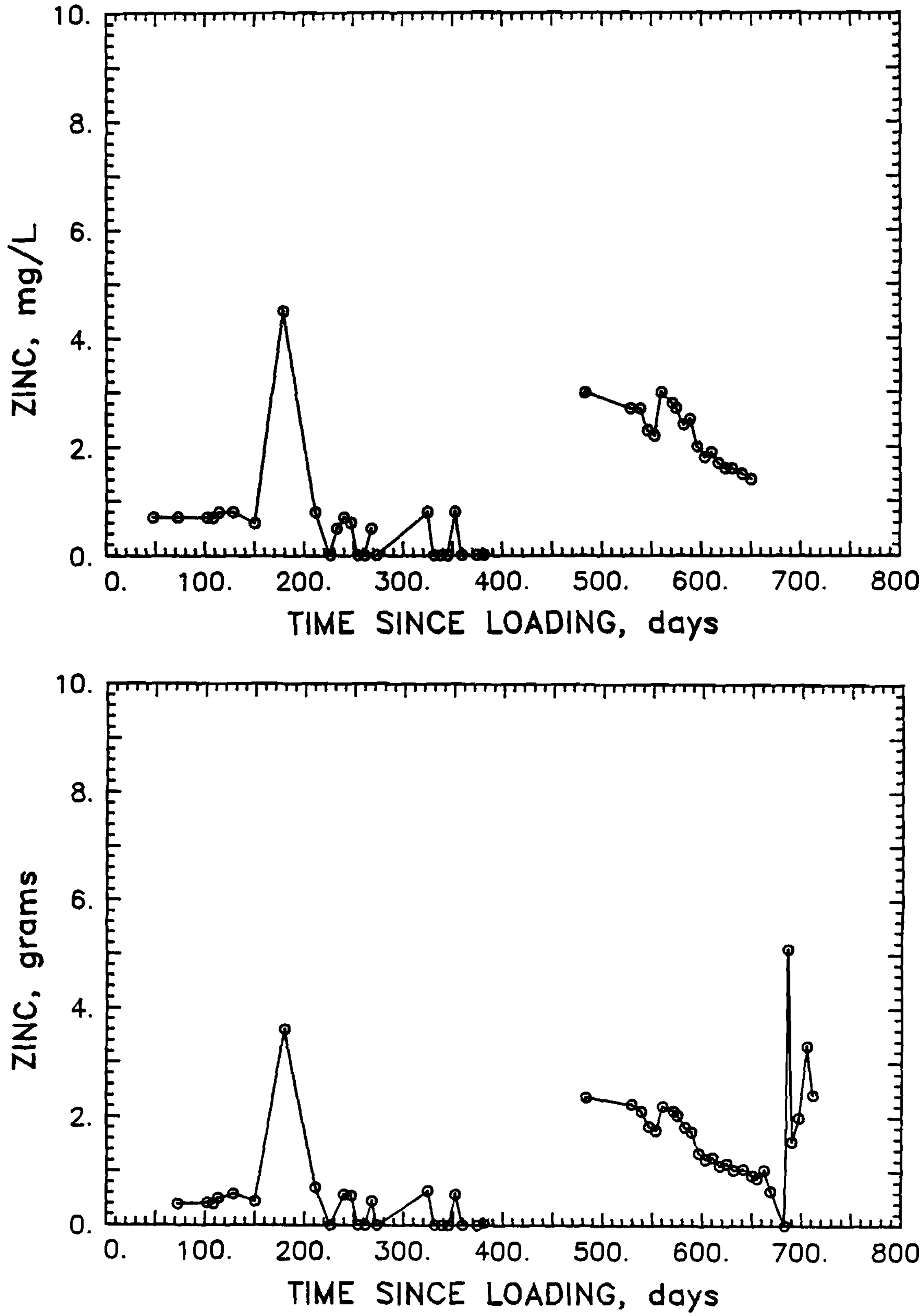


Figure 17. Zinc Content of Column 1 Leachate

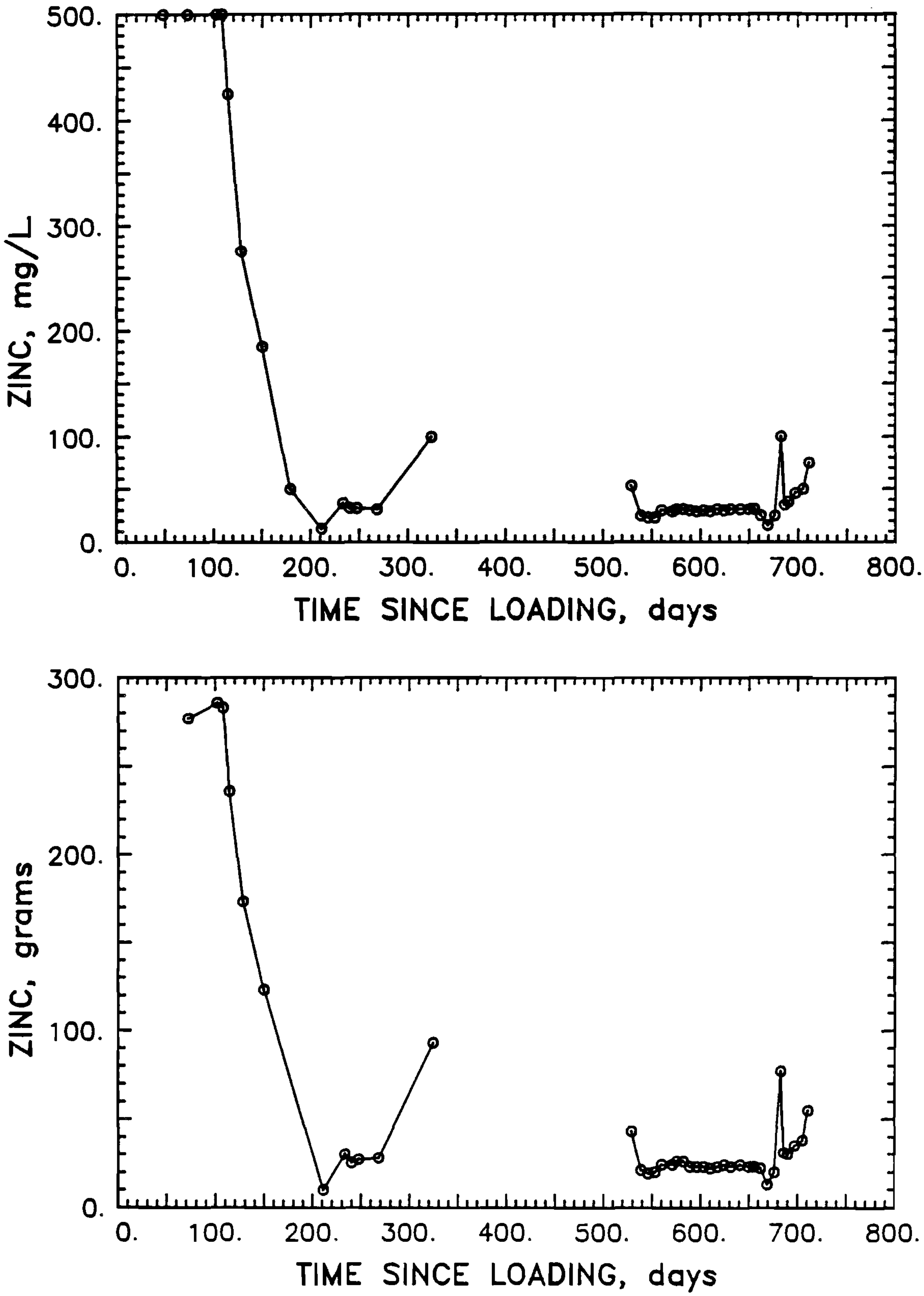


Figure 18. Zinc Content of Column 2 Leachate

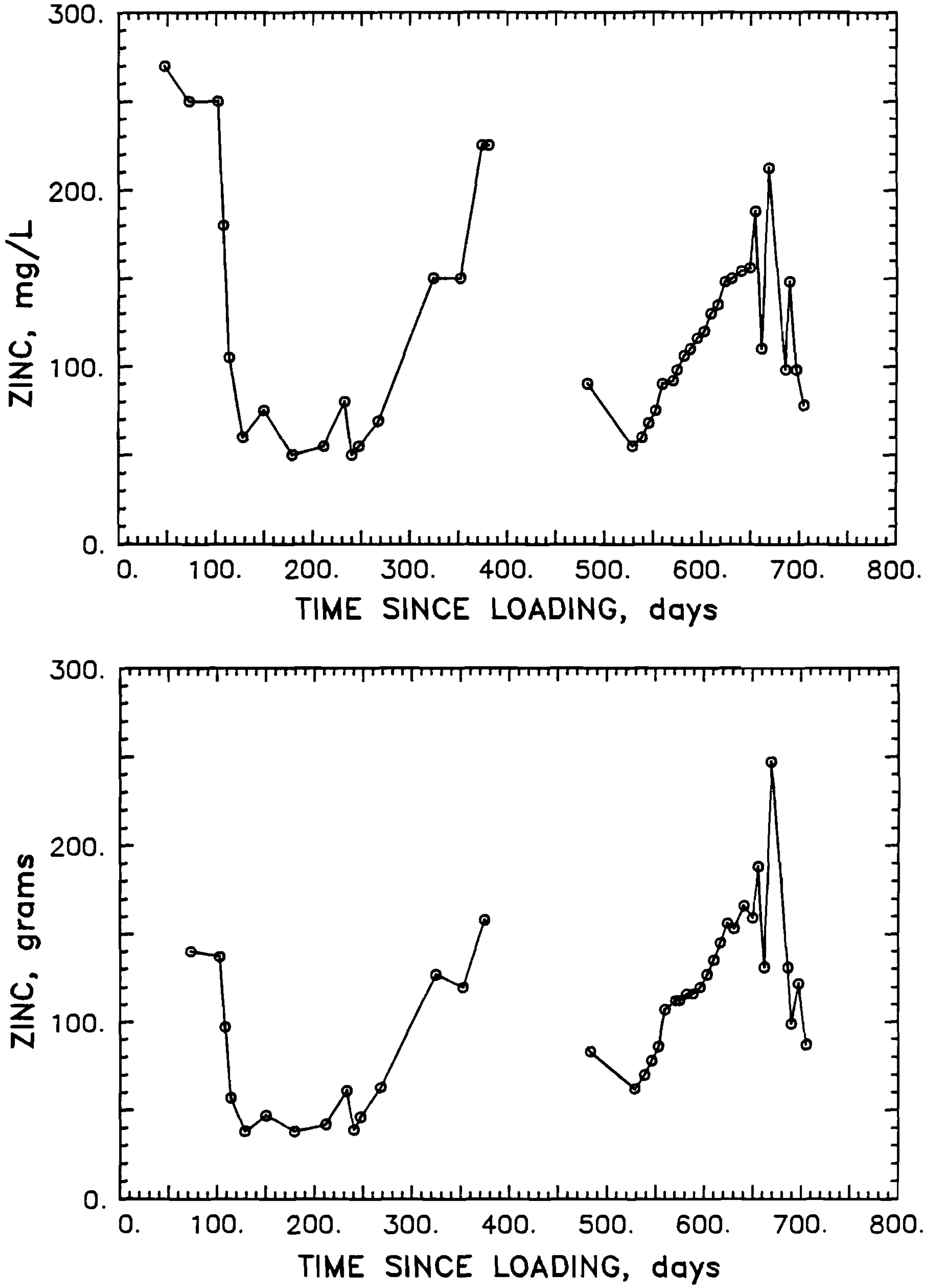


Figure 19. Zinc Content of Column 3 Leachate

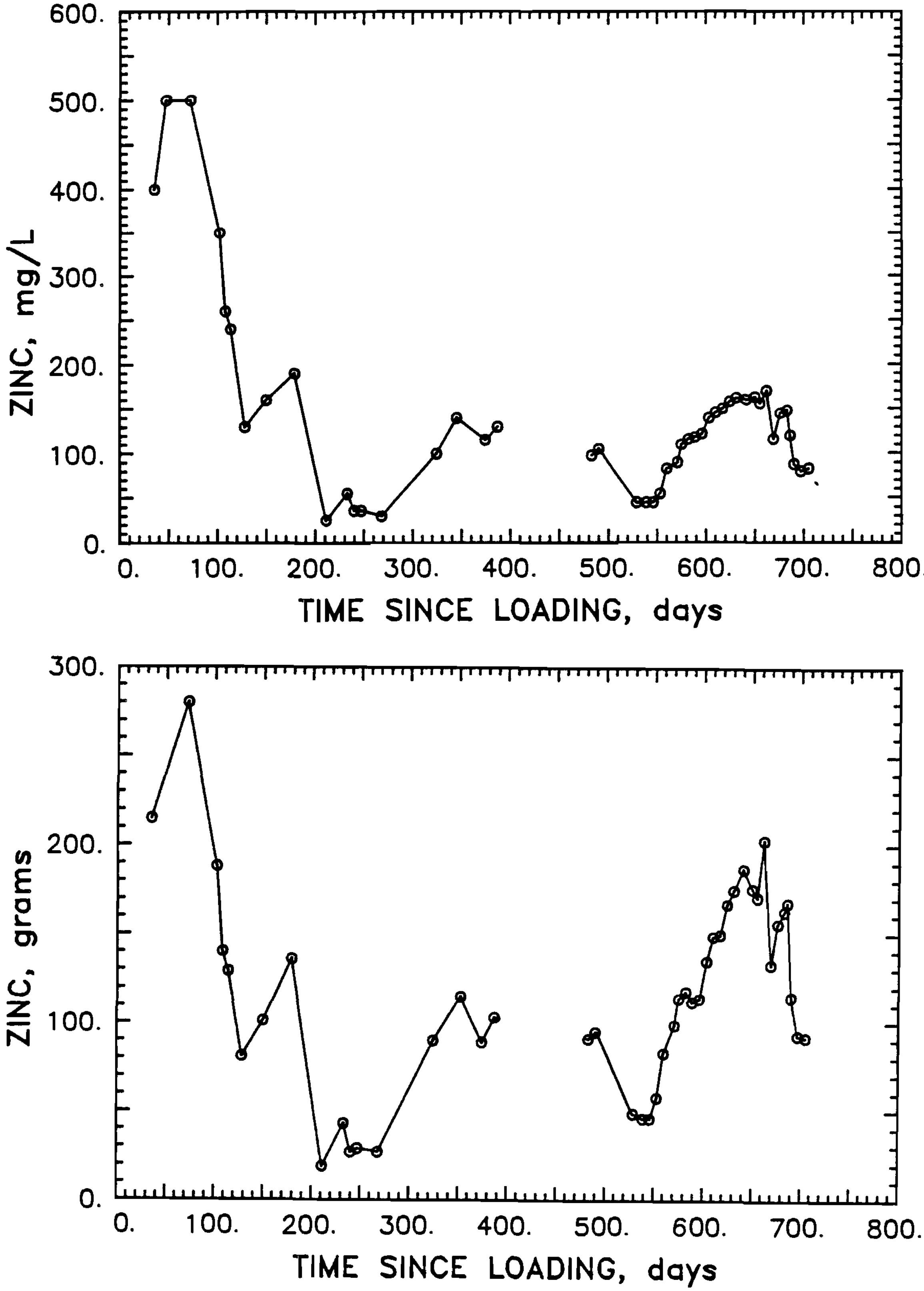


Figure 20. Zinc Content of Column 4 Leachate

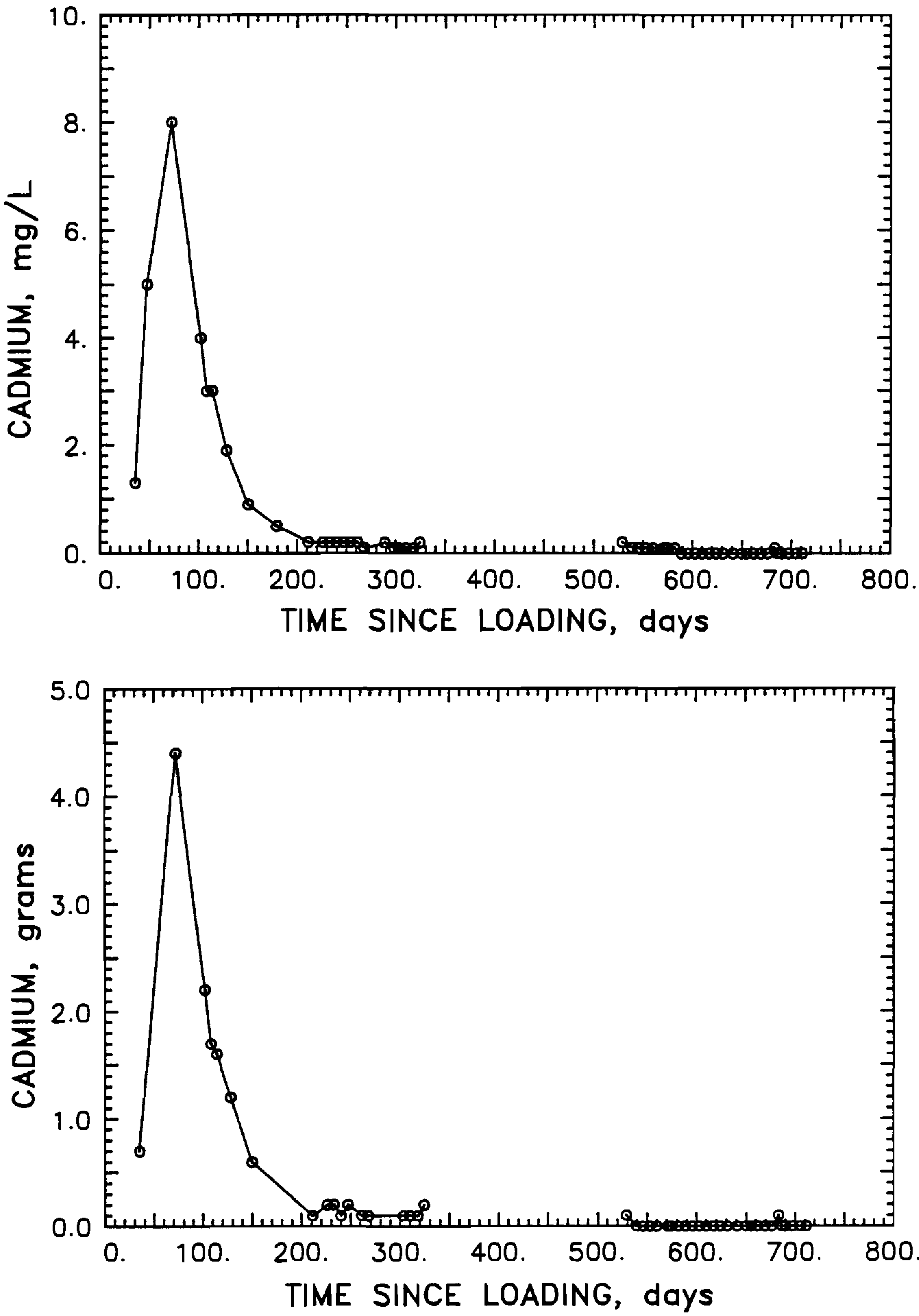


Figure 21. Cadmium Content of Column 2 Leachate

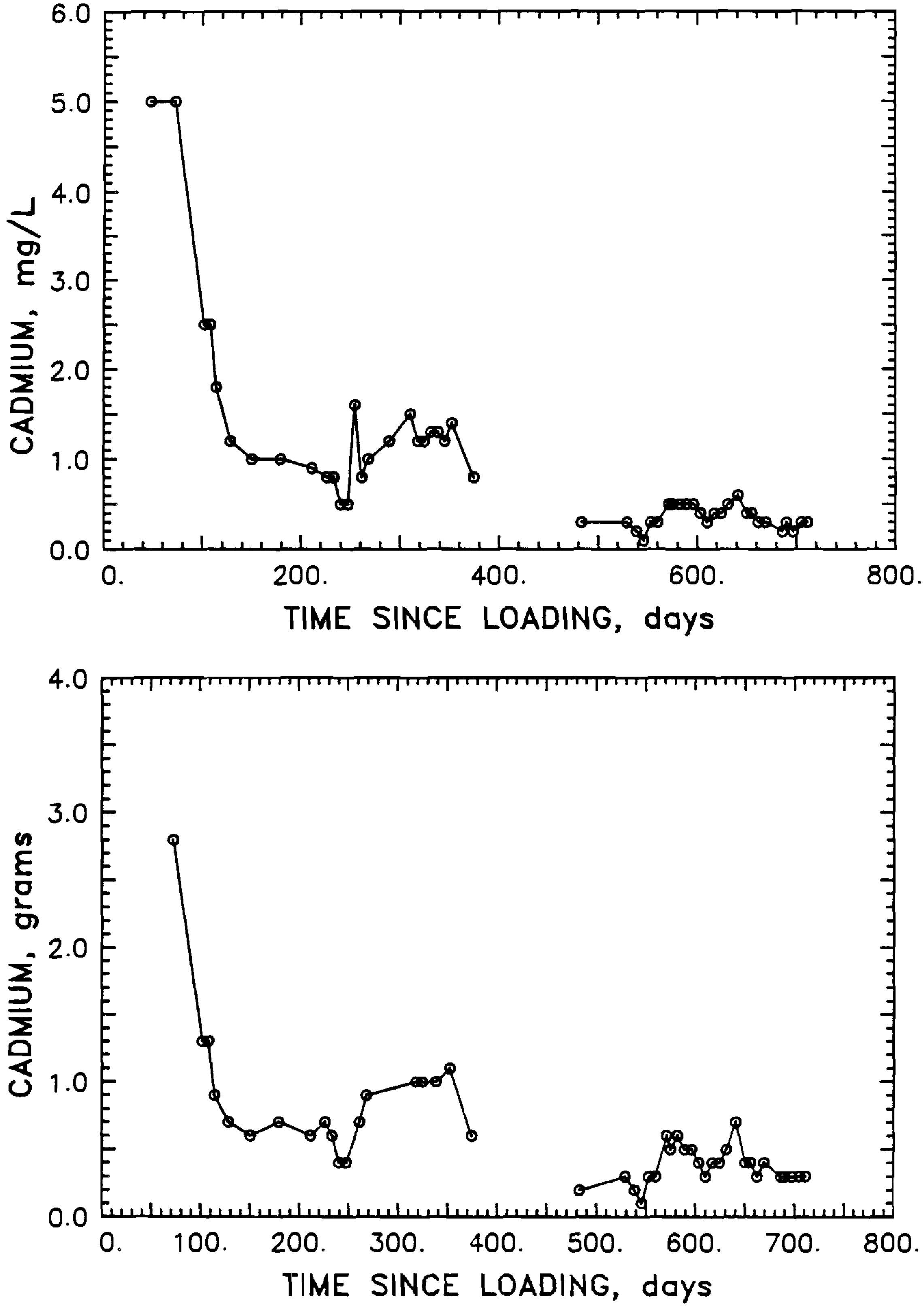


Figure 22. Cadmium Content of Column 3 Leachate

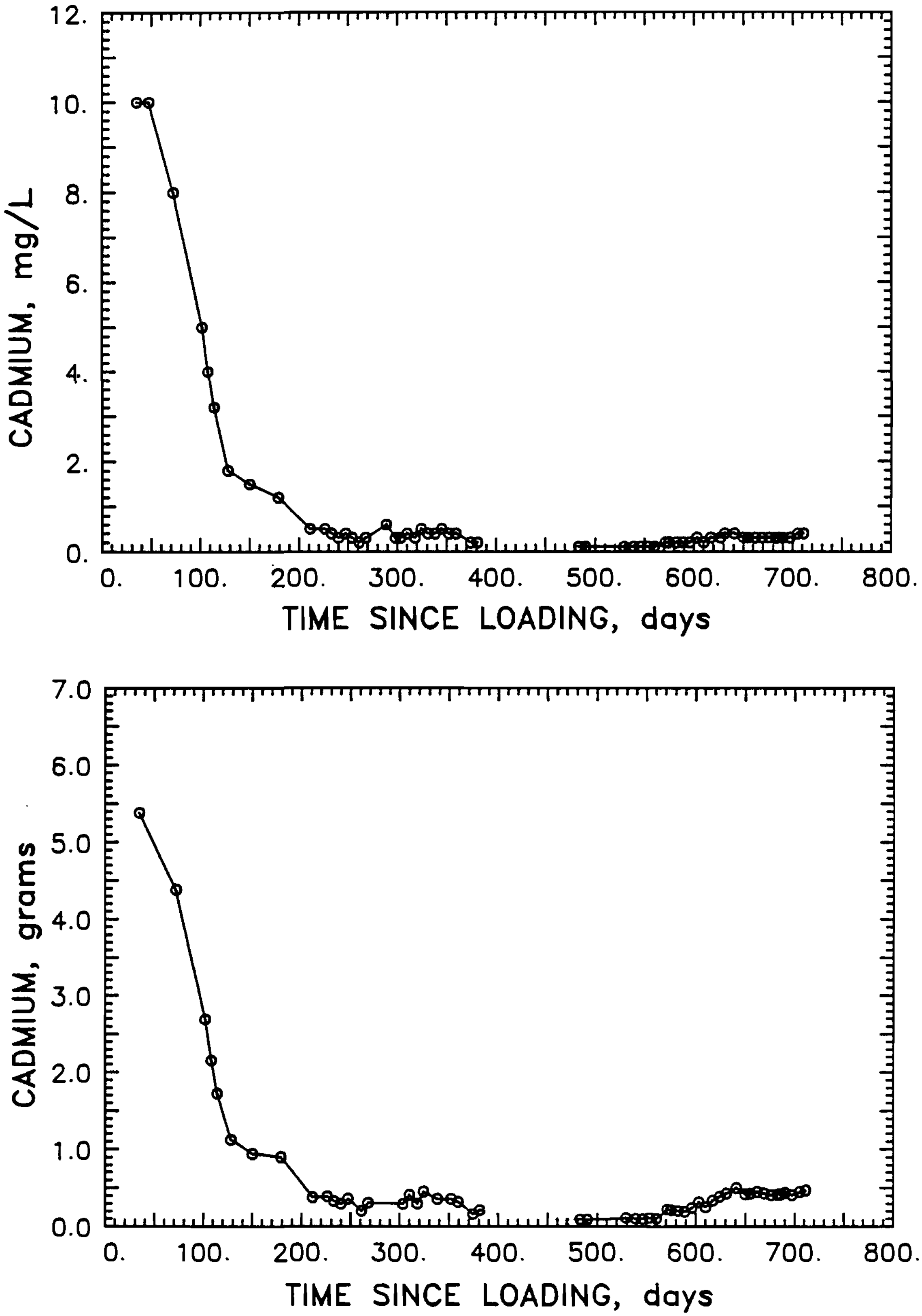


Figure 23. Cadmium Content of Column 4 Leachate

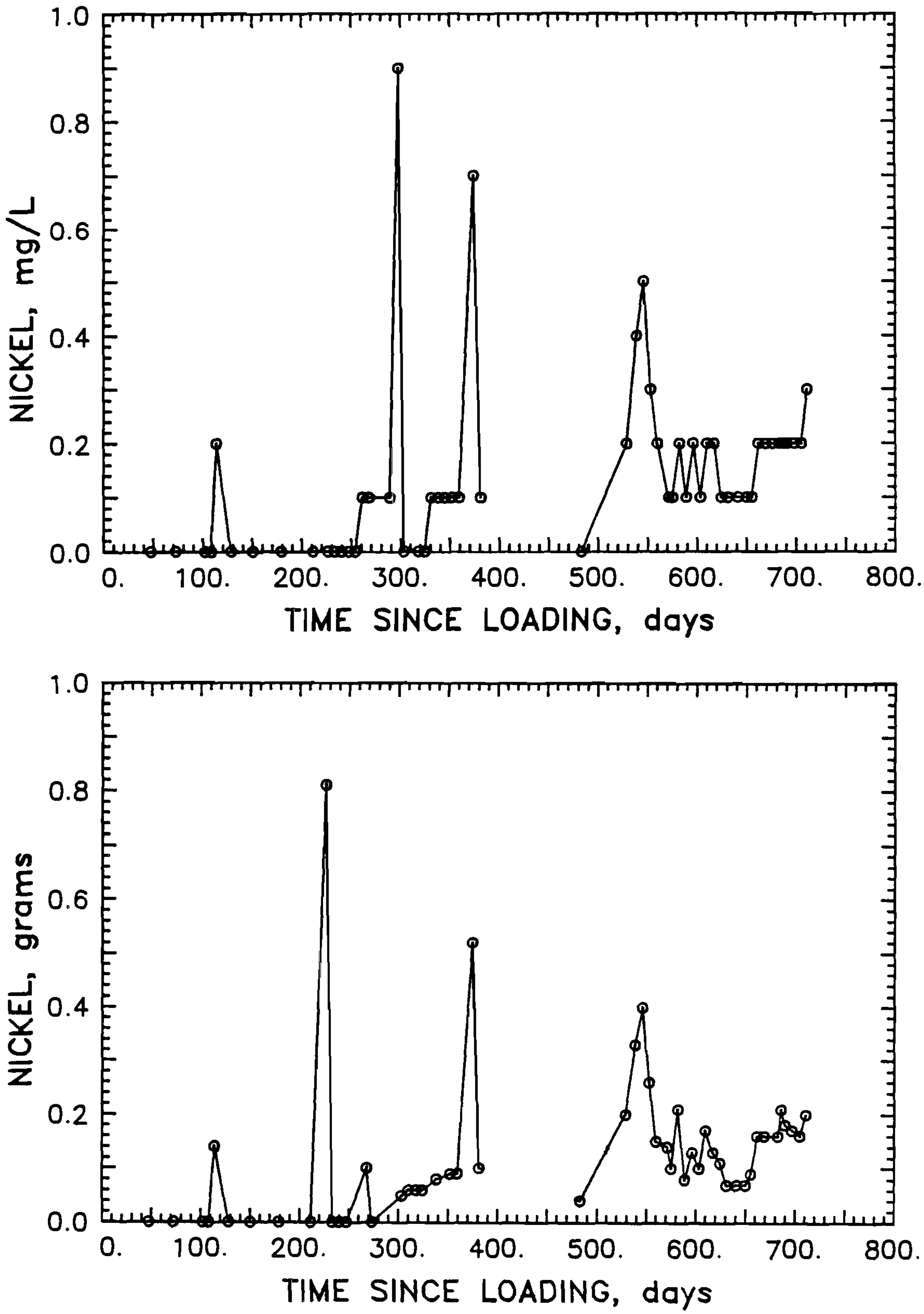


Figure 24. Nickel Content of Column 1 Leachate

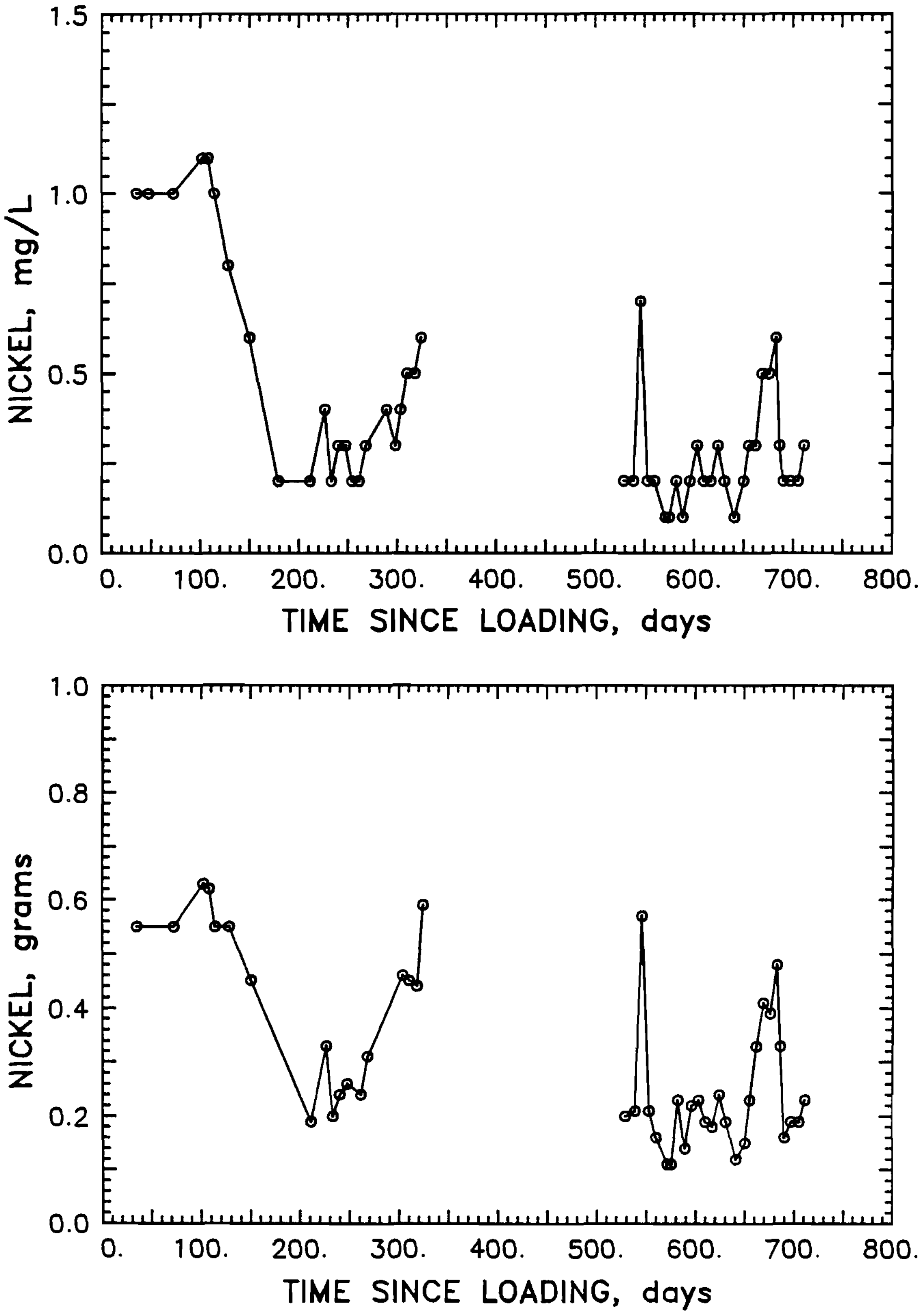


Figure 25. Nickel Content of Column 2 Leachate

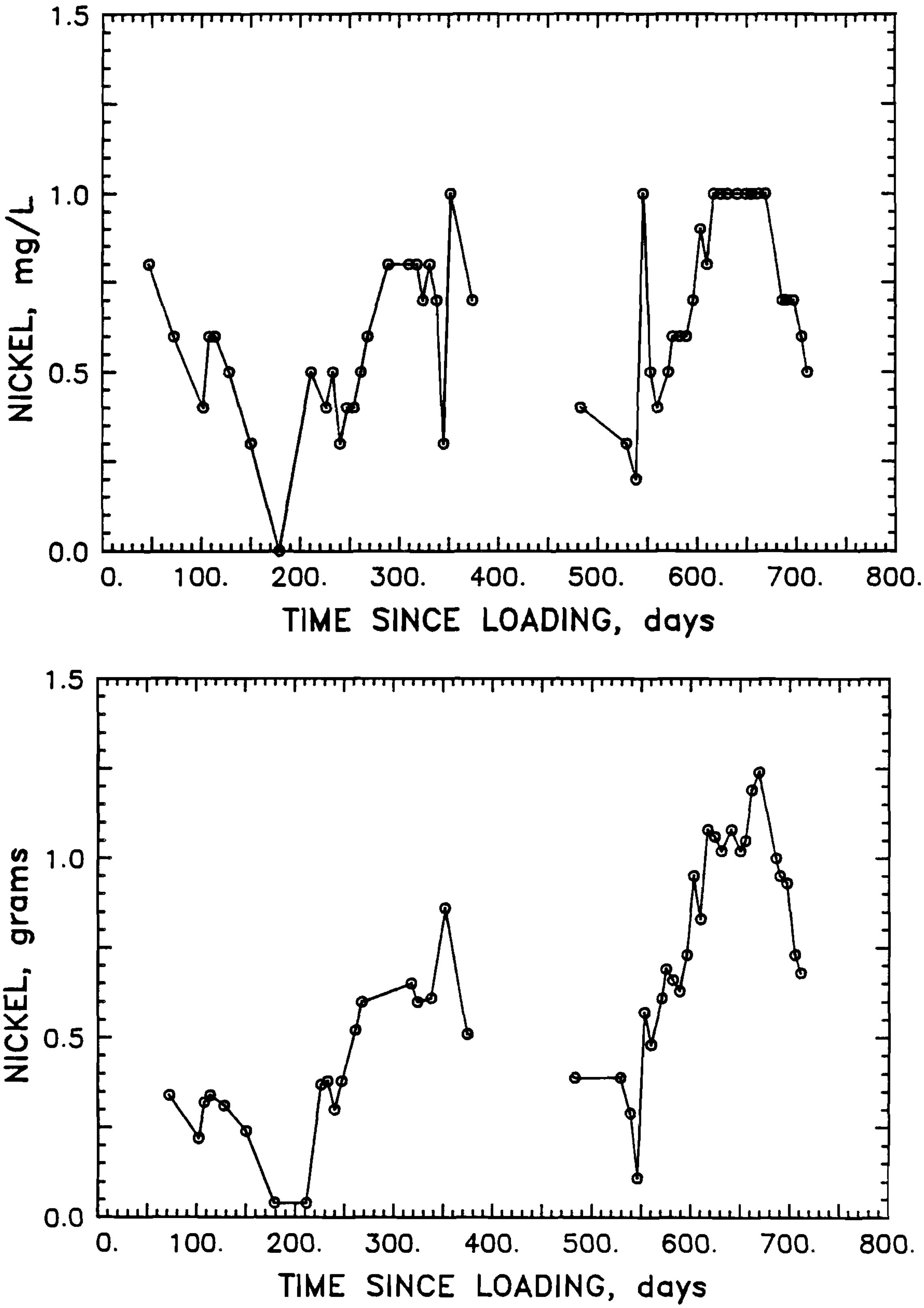


Figure 26. Nickel Content of Column 3 Leachate

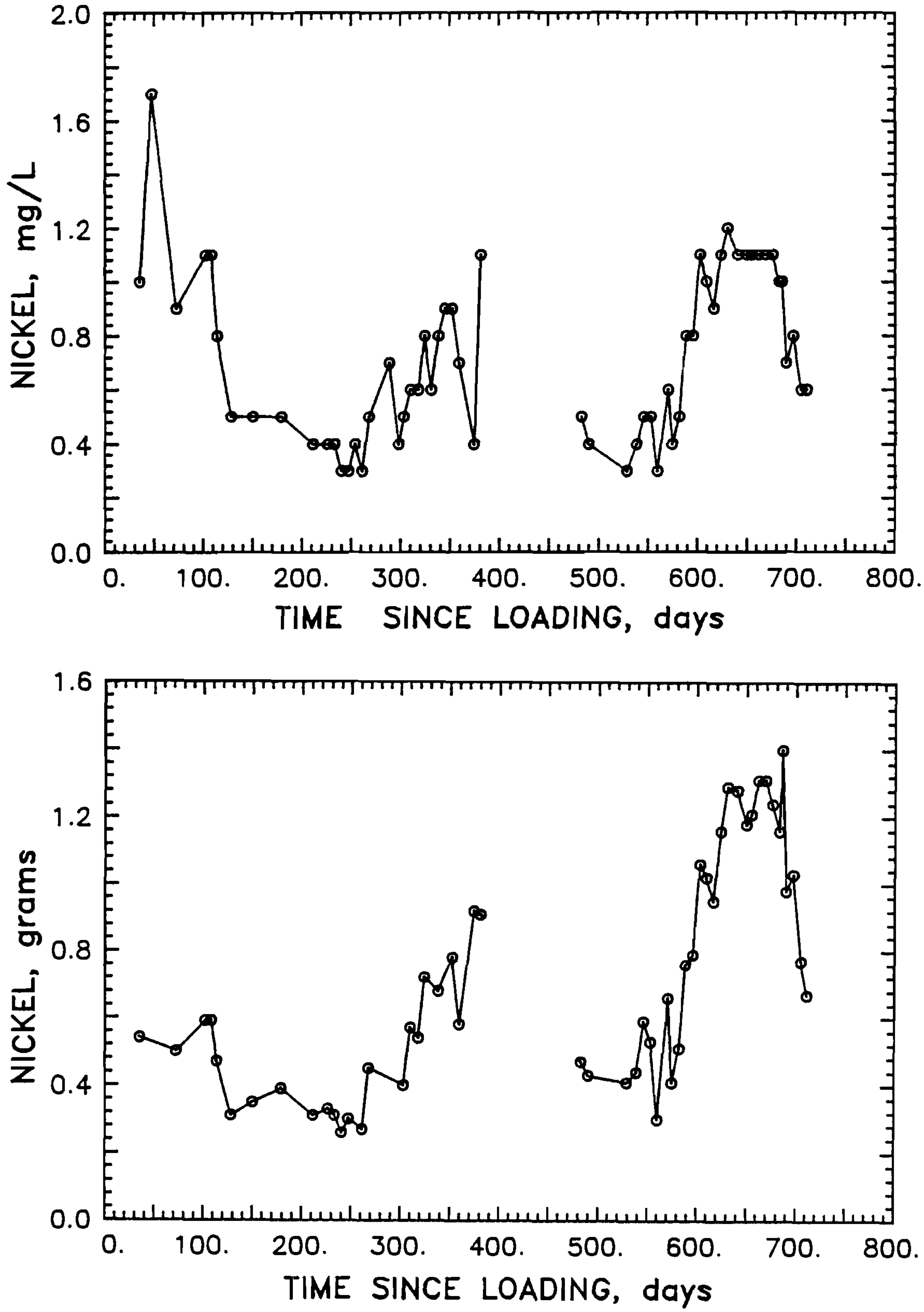


Figure 27. Nickel Content of Column 4 Leachate

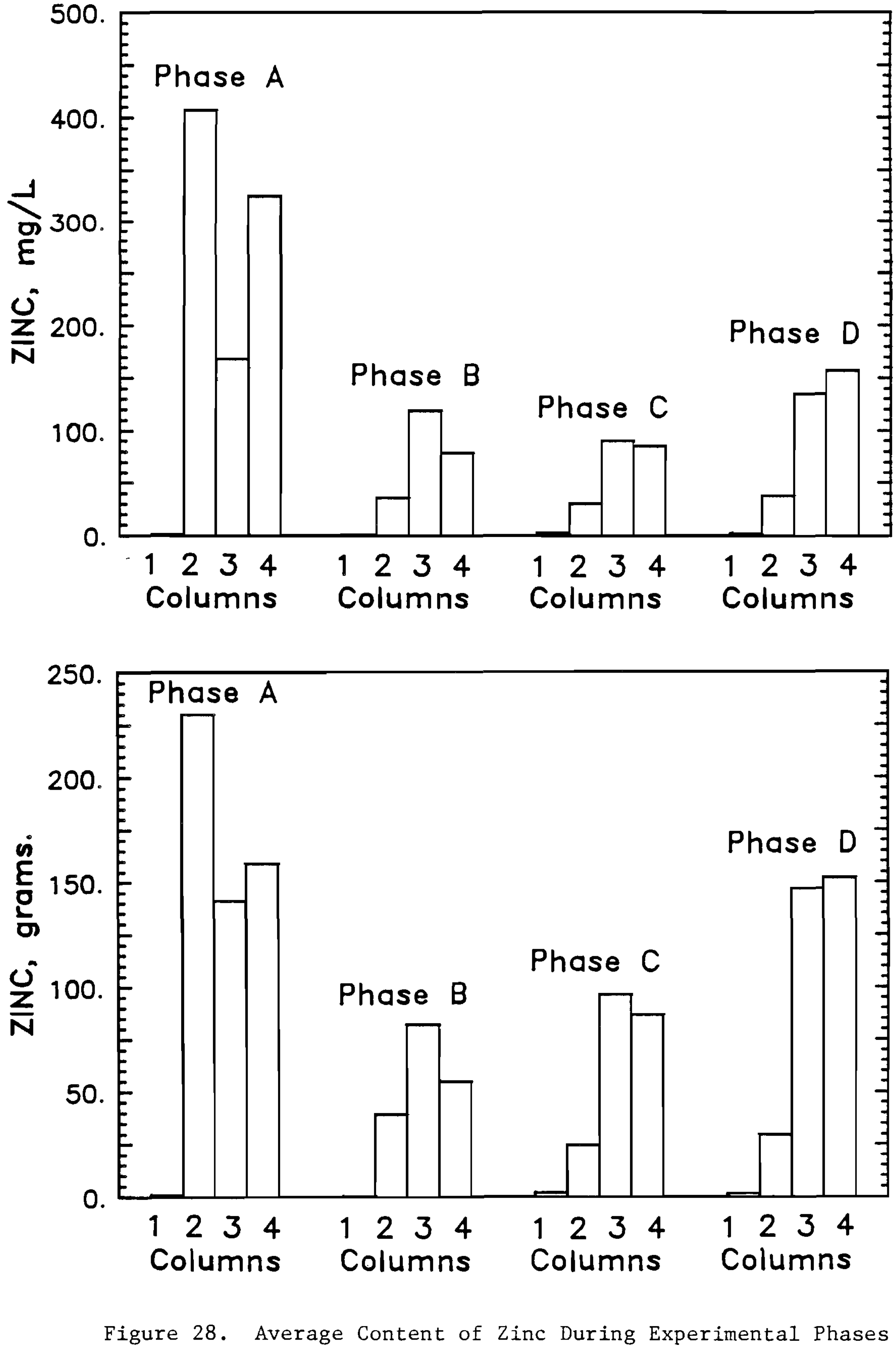


Figure 28. Average Content of Zinc During Experimental Phases

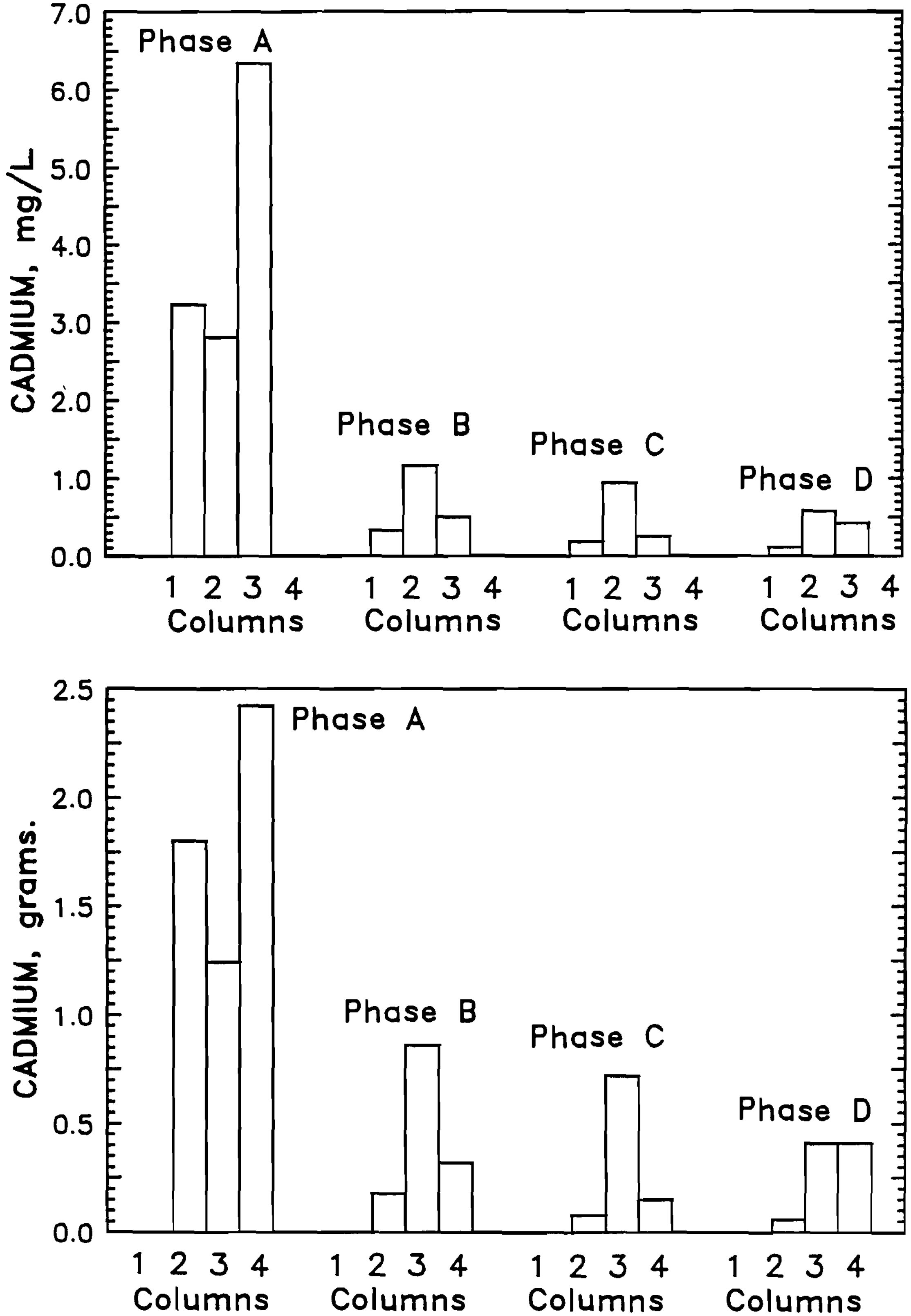


Figure 29. Average Content of Cadmium During Experimental Phases

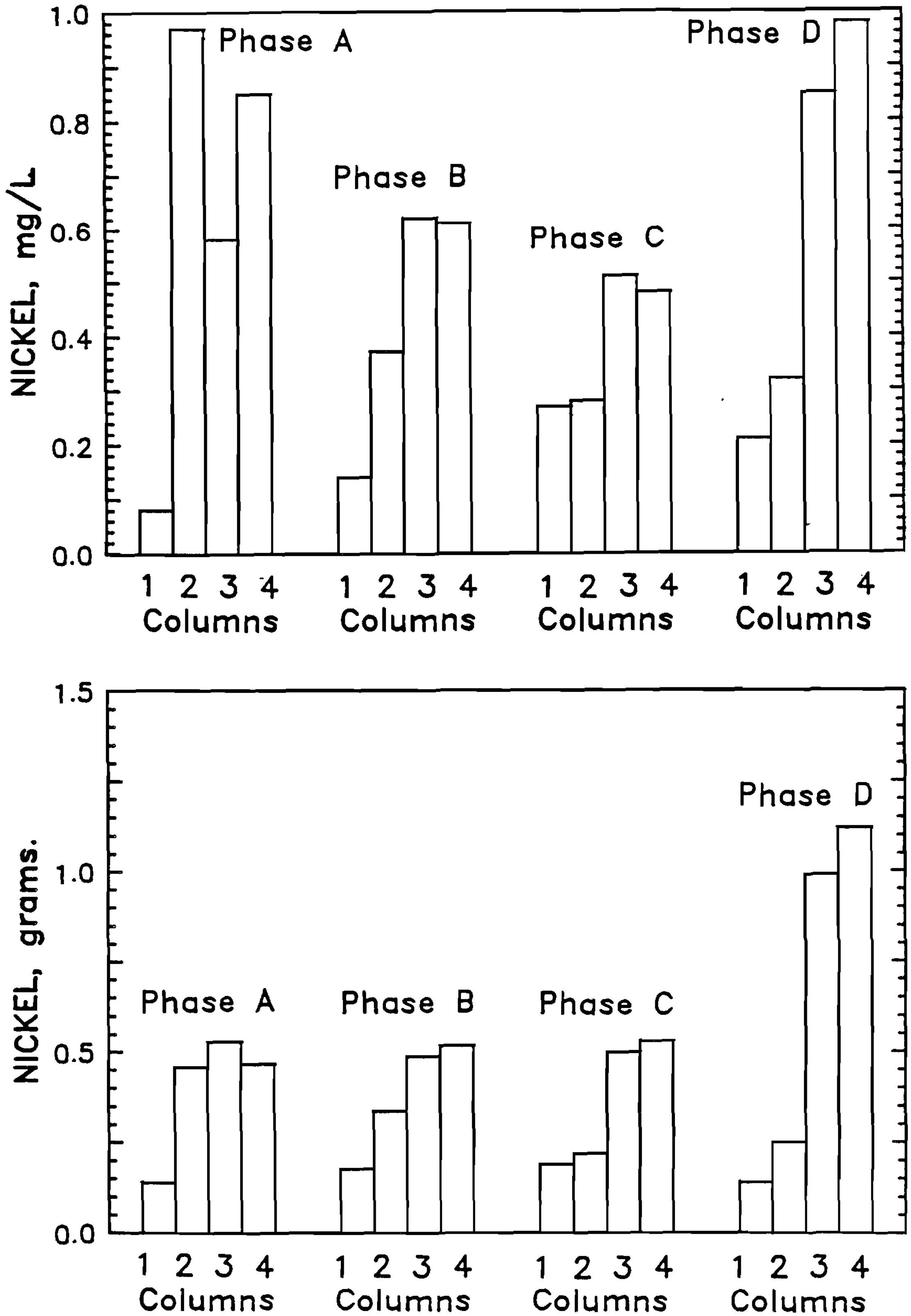


Figure 30. Average Content of Nickel During Experimental Phases

significant degree of fixation, no doubt enhanced by the early onset of anaerobic reducing conditions and the production of metal precipitating sulfides (Tables 13-16). These reducing conditions remained in effect during the drought period, thereby helping to maintain the availability of sulfides and further restricting metal mobility. Eventually, however, in the final stages of the investigations, the chemical environment became more conducive to enhanced heavy metal mobilities as will be discussed in detail later.

Changes in Chemical Oxygen Demand with Time--

Of the various parameters employed during these investigations, chemical oxygen demand (COD) provided the best overall measure of the changes in the total array of organic compounds present in the leachate. It is likely that the bulk of the theoretical oxygen demand of the organic compounds in the leachates was measured by this analysis. The major source of any potential uncertainty will be the positive interference resulting from the presence of such reduced inorganic compounds as ferrous iron and sulfide. However, this interference was not considered sufficient to obscure trends in COD accountable to the organic compounds.

The temporal variations of COD in the leachate from the simulated landfill columns are shown in Figures 31 through 34. As with the changes in heavy metals, leachate COD levels for Column 1 showed a normal pattern of rapid initial washout/microbially mediated stabilization and an establishment of an essentially constant level after approximately 200 days of column operation. This constant level was then maintained essentially unchanged for the duration of the study, apparently uninfluenced by the extended period of drought. Column 2, which contained the lowest metal sludge loading, demonstrated a behavior quite similar to that of Column 1 except for increases in leachate COD levels immediately prior to the cessation of leachate production and again, but to a lesser extent, very late in the course of the investigations. For Columns 3 and 4, the trends in leachate COD were very similar with an initial washout being followed by a significant increase in COD which peaked shortly before the drought-induced cessation of leachate production. Upon resumption of leachate production, the COD leachate levels for these columns decreased very substantially with respect to those observed immediately prior to the drought period. Thereafter, leachate COD values increased steadily and showed evidence of reaching and then starting to recede from a peak value immediately prior to termination of column operation. Collectively, these variations were strongly suggestive of a cyclic process which may have resulted from alternating periods of toxicity/inhibition and acclimation in those columns containing the highest levels of metal sludge.

Using the general chronology established previously (Table 17), four more or less similar but discrete experimental phases were observed for COD as listed in Table 18. The corresponding average of the leachate COD levels in the landfill columns are shown graphically in Figure 35. Scrutiny of the data presented in this figure tends to confirm the trends inferred in the concentration and mass versus time plots (Figures 31 through 34). Thus, the rapid washout and stabilization in Column 1 is readily evident, while the apparent cyclic behavior of Columns 3 and 4 can also be observed. The data of Figure 35 also show clearly the transitional nature of Column 2 whose behavior was consistantly intermediate between that of Column 1 and the trends displayed by Columns 3 and 4.

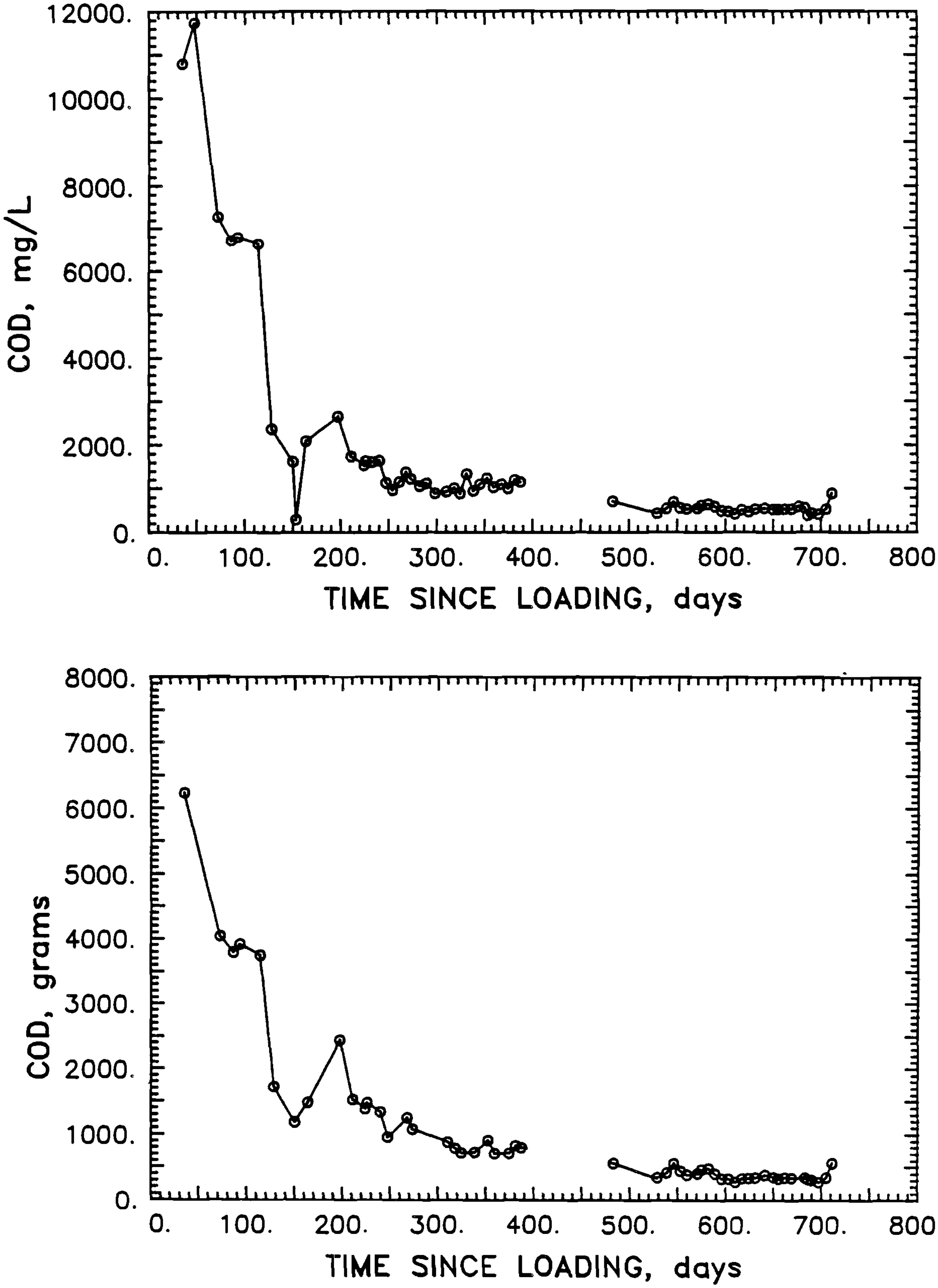


Figure 31. Chemical Oxygen Demand of Column 1 Leachate

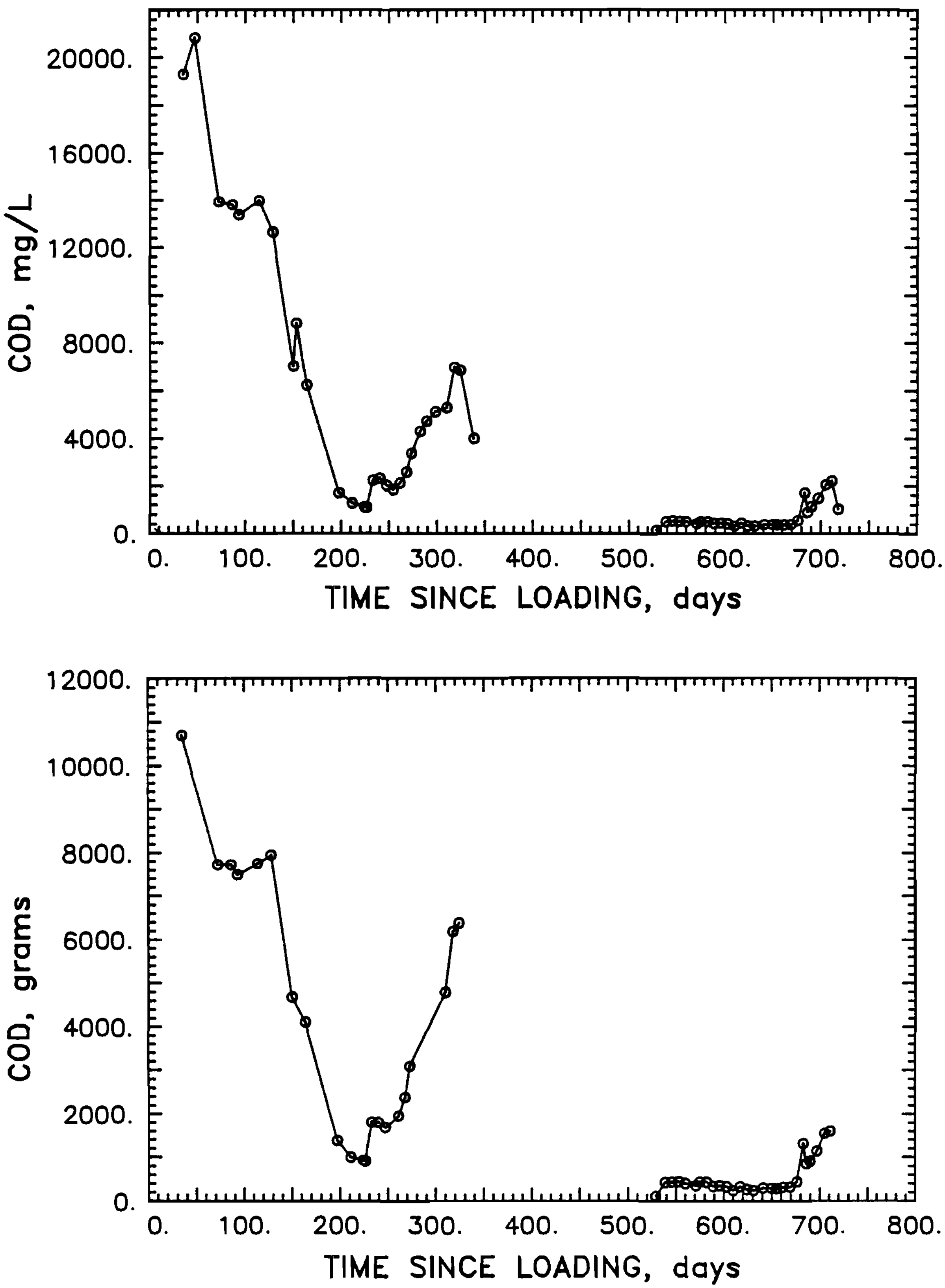
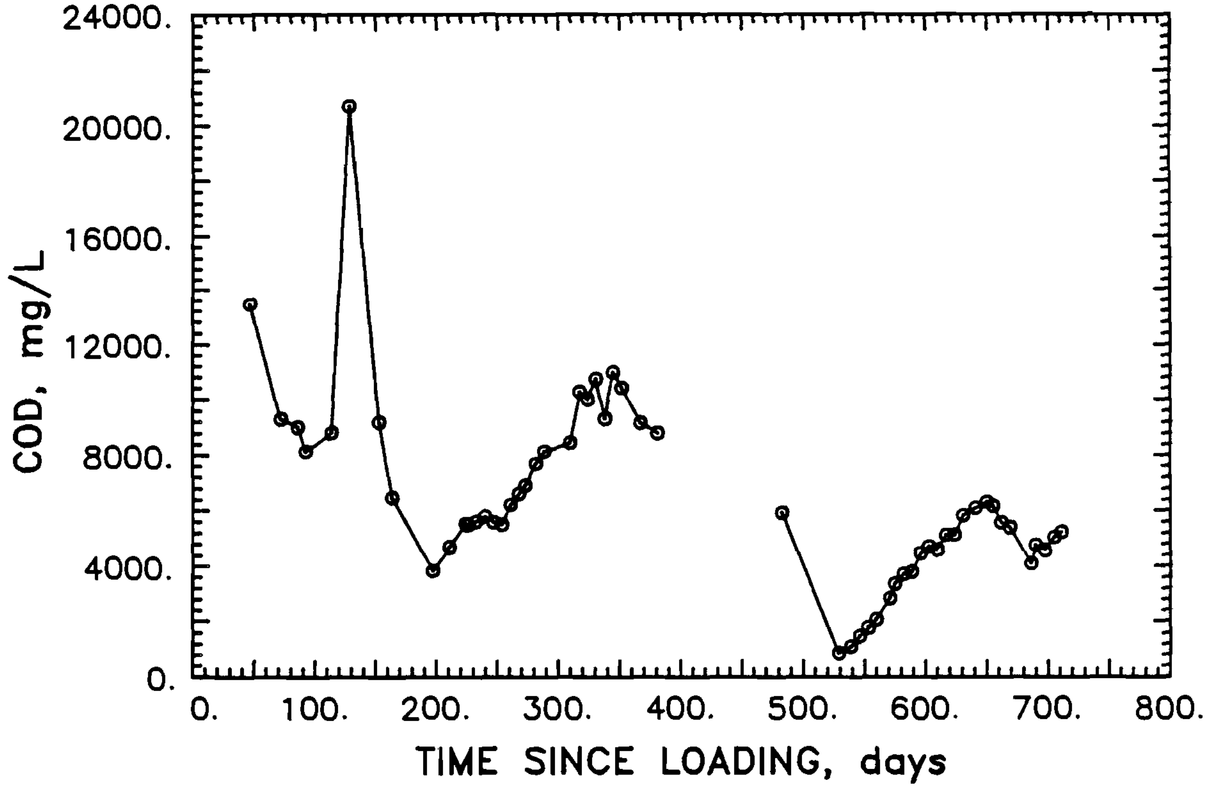


Figure 32. Chemical Oxygen Demand of Column 2 Leachate



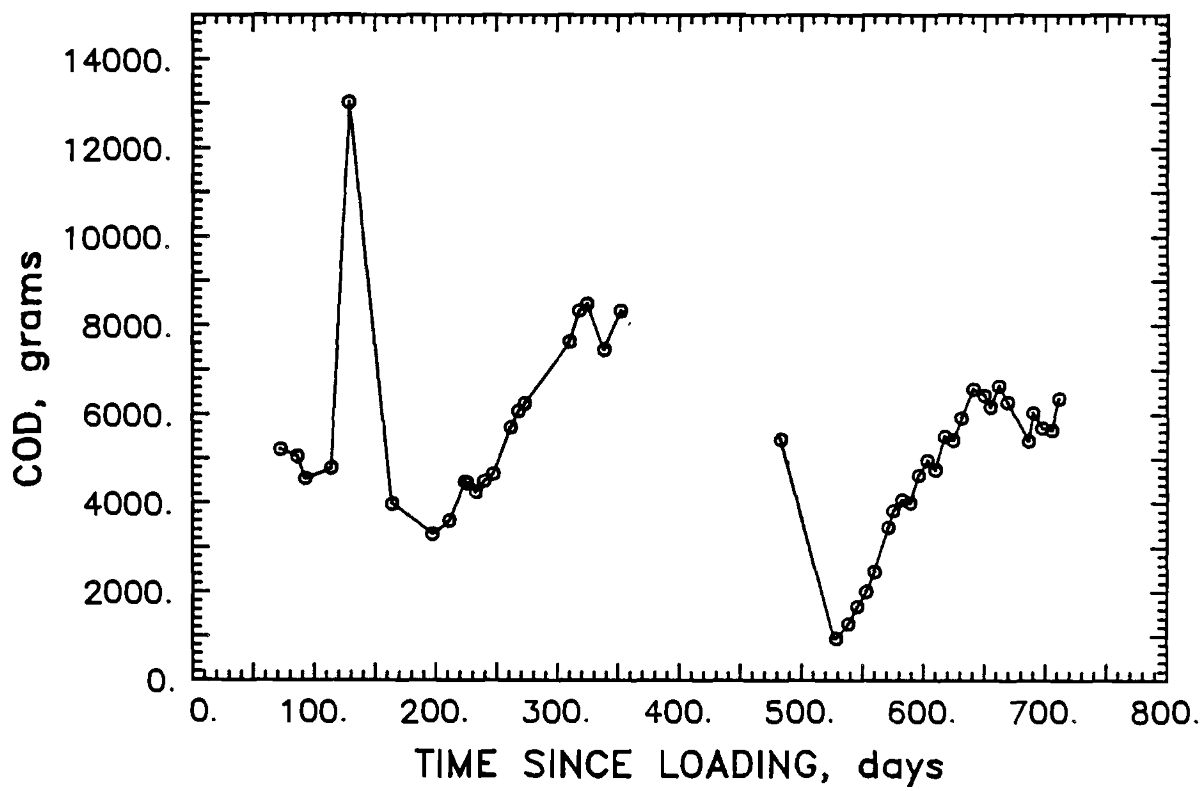


Figure 33. Chemical Oxygen Demand of Column 3 Leachate

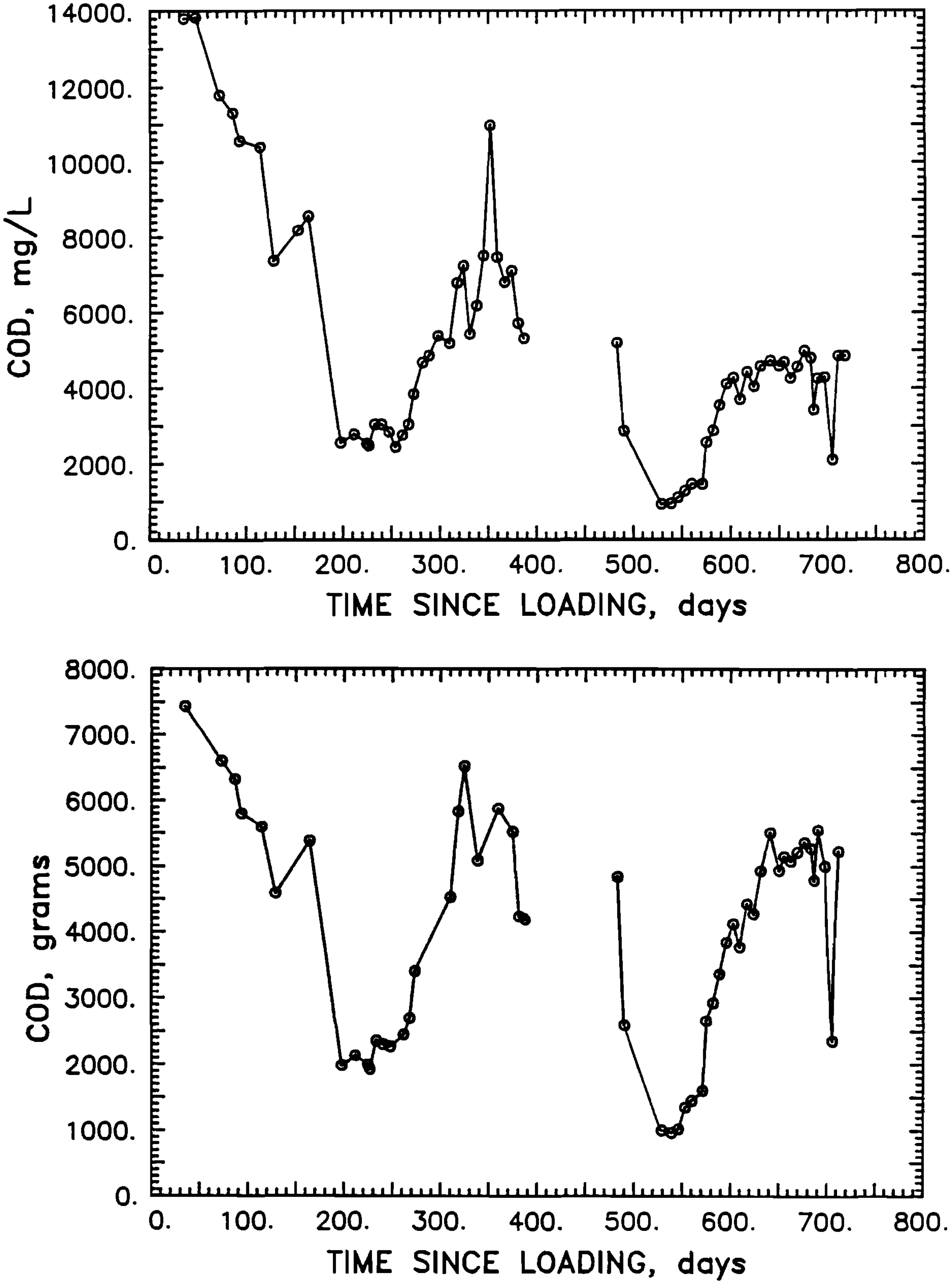


Figure 34. Chemical Oxygen Demand of Column 4 Leachate

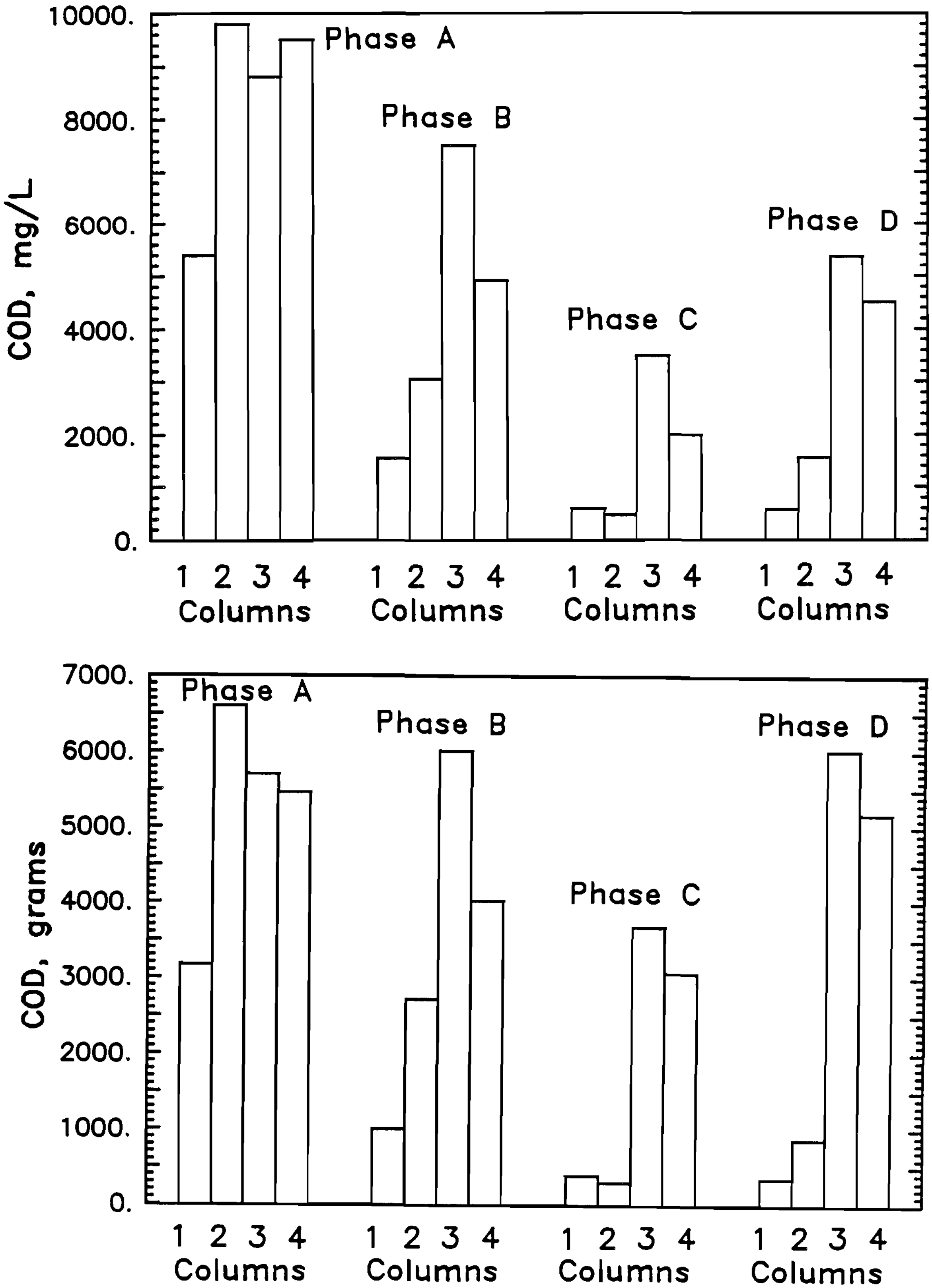


Figure 35. Average Chemical Oxygen Demand During Experimental Phases

TABLE 18. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR CHEMICAL OXYGEN DEMAND ANALYSES

Experimental Phase	Days	Operational Characteristics
A	0-200	Washout
B	200-400	Initial stabilization
C	530-650	Post-drought
D	650-730	Terminal

Changes in Biochemical Oxygen Demand with Time--

During the early phases of this research, the primary measure of organic content in the leachates was the COD. Thus, very few biochemical oxygen demand (BOD_5) measurements were performed during the pre-drought period. However, in an effort to evaluate the impact of the sludge metals on the biodegradability of leachate organic fractions, the frequency of BOD_5 measurements was substantially increased during the latter half of the experimental period. As a result, although the BOD_5 data during the study period prior to the drought are insufficient to permit any conclusive interpretations of early trends, signficiant conclusions can be drawn concerning the behavior of BOD_5 during the last half of the research period.

Perhaps the most significant feature of the BOD_5 data (Figures 36 through 39) is the nearly exact correspondence between the changes in BOD_5 and the previously described changes in COD (Figures 31 through 34) during the post-drought period of column operation. The similarity of behavior of Column 2 leachate to that of the control column (Column 1) once again indicated the capacity of these landfills to adapt to the level of metal sludge contained in Column 2 with little evidence of inhibition of biological activity. In contrast, the leachate from Columns 3 and 4 displayed strong evidence of inhibition in terms of BOD_5 patterns and some indication of the onset of a cyclic process of alternating biological activity and inhibition.

Based on these data, it appears that leachate COD provided a valid measure of the gross organic content of the leachate and yielded results corresponding closely to those obtained by consideration of BOD_5 data. These results also indicated that, while the higher levels of metal sludge in Columns 3 and 4 significantly inhibited biological activity in these columns, the inherent degradability of the organic compounds in these leachates was not reduced to any significant extent once removed from the influences of the metal. This suggests that leachates generated in localized regions of high metal sludge loading in a larger landfill will be amenable to treatment by uninhibited biological communities in other portions of the landfill.

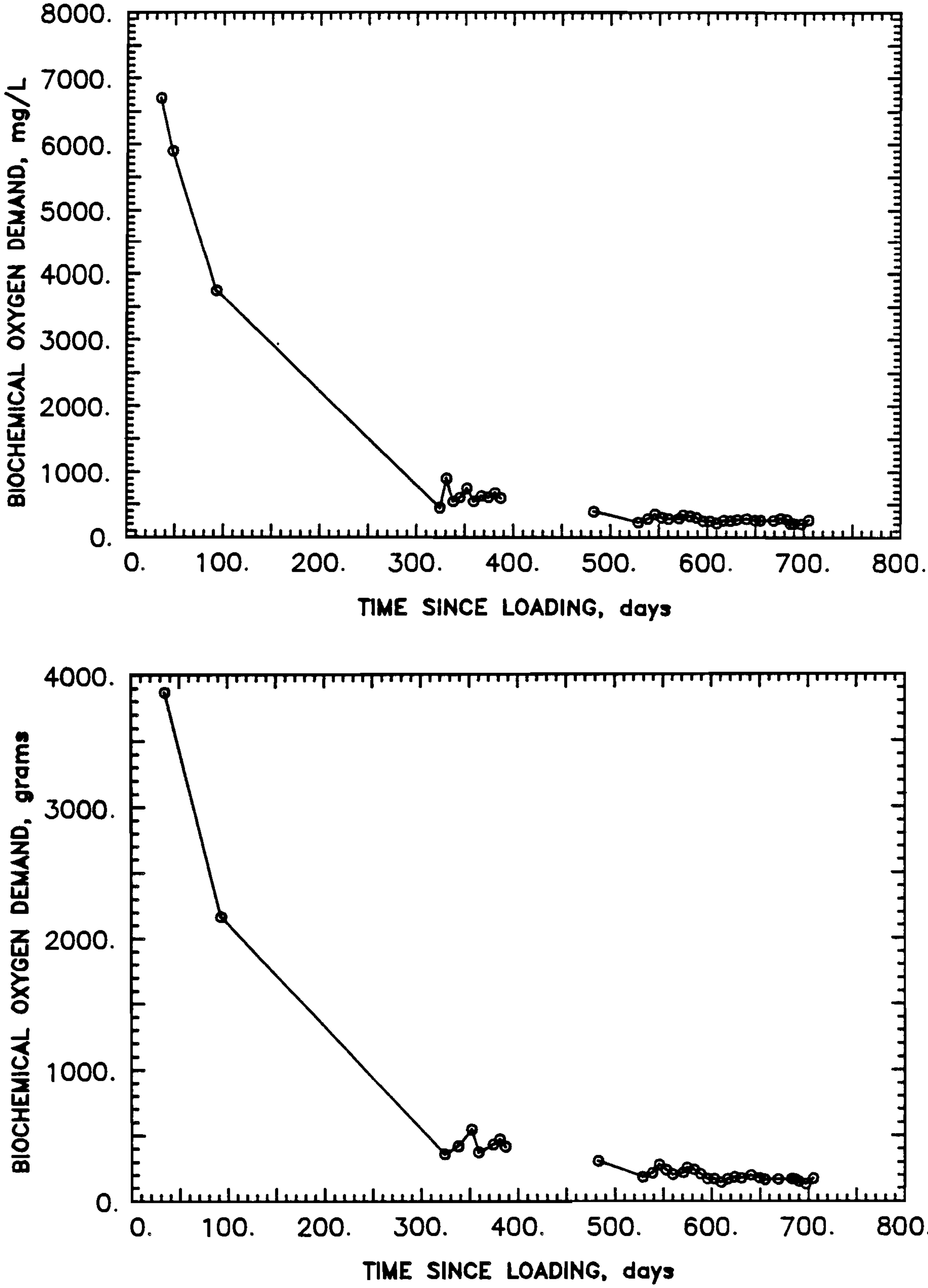


Figure 36. Biochemical Oxygen Demand of Column 1 Leachate

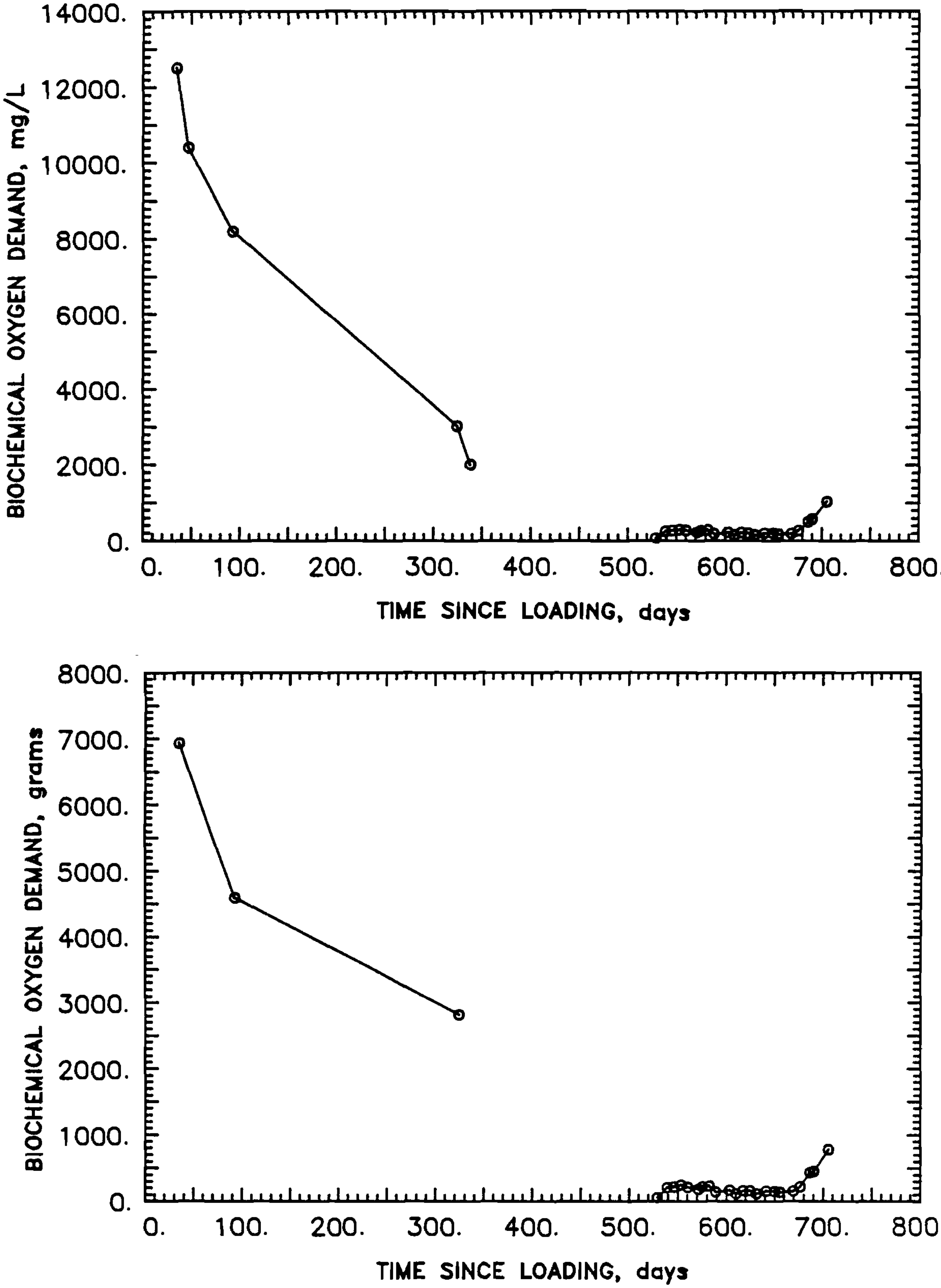


Figure 37. Biochemical Oxygen Demand of Column 2 Leachate

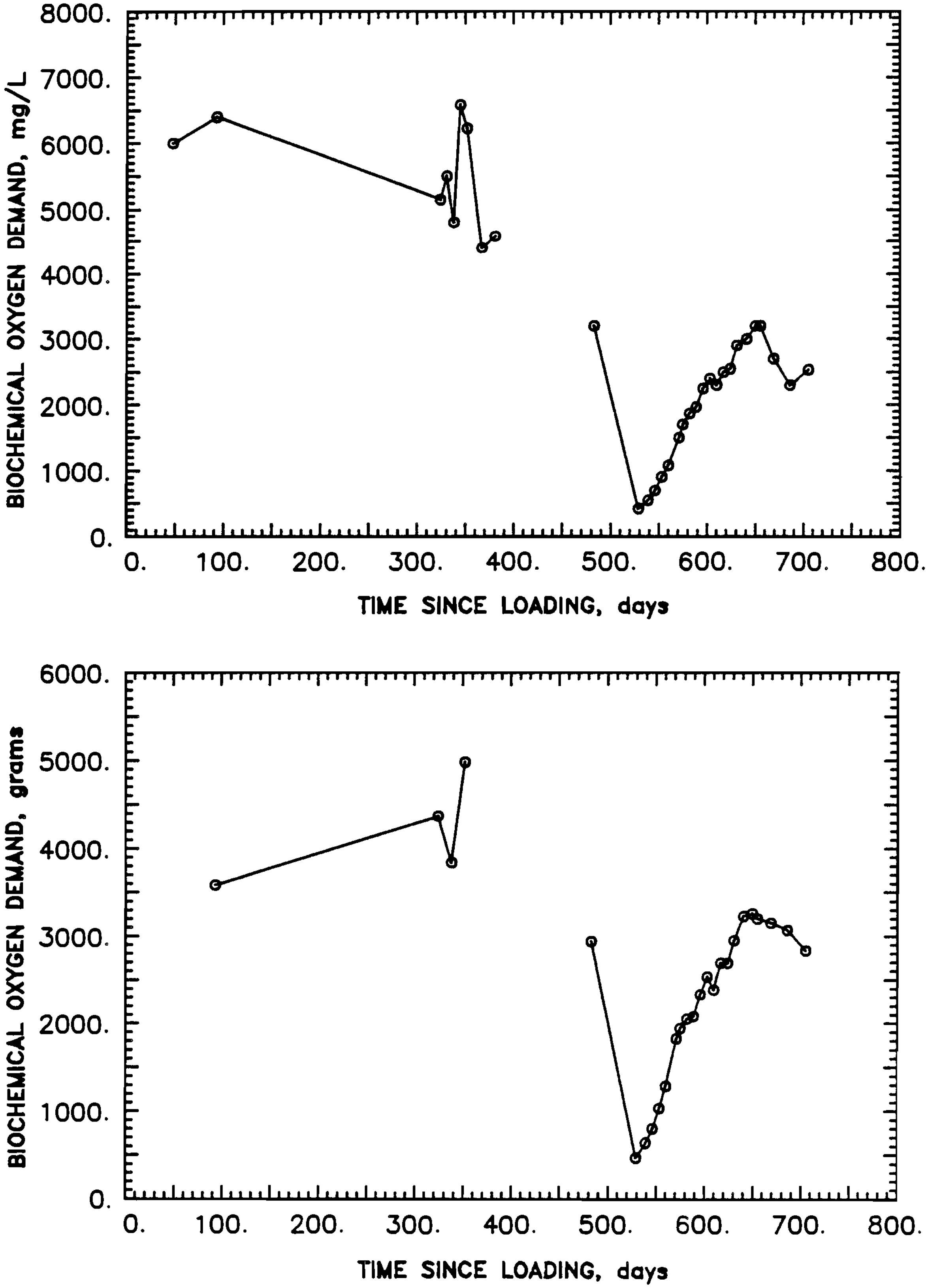
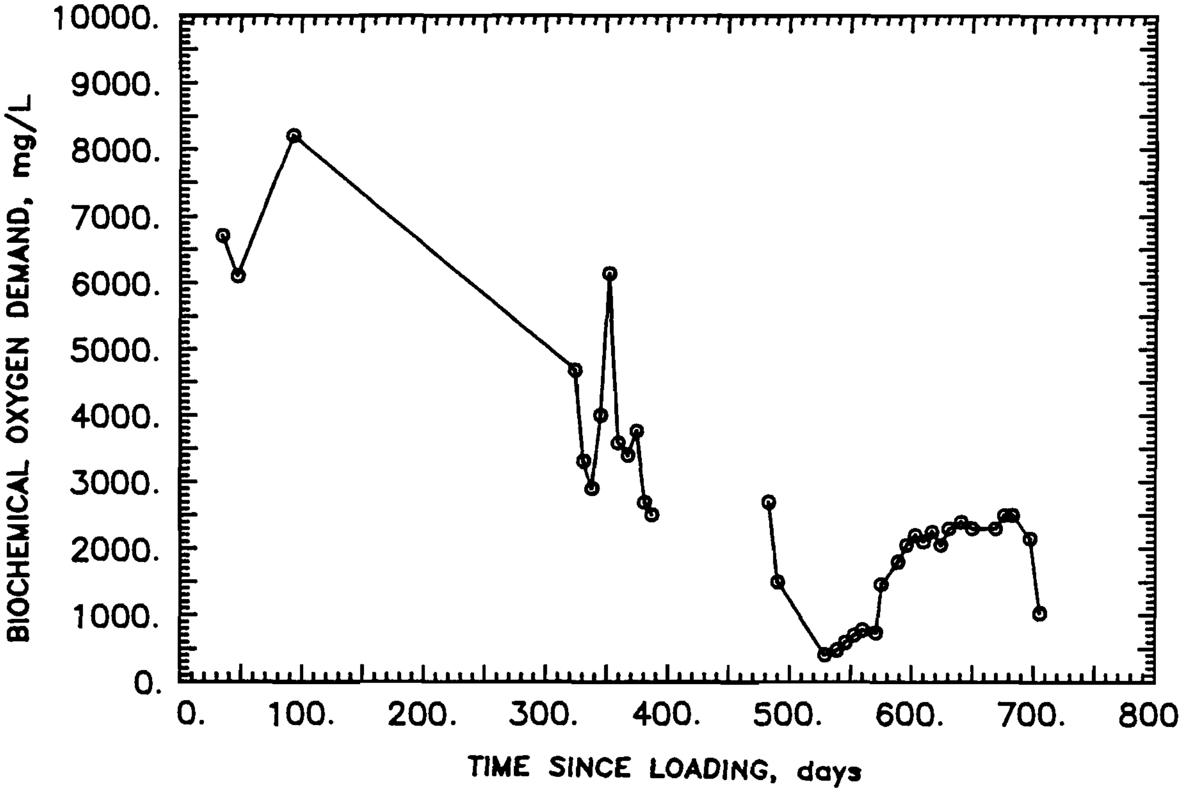


Figure 38. Biochemical Oxygen Demand of Column 3 Leachate



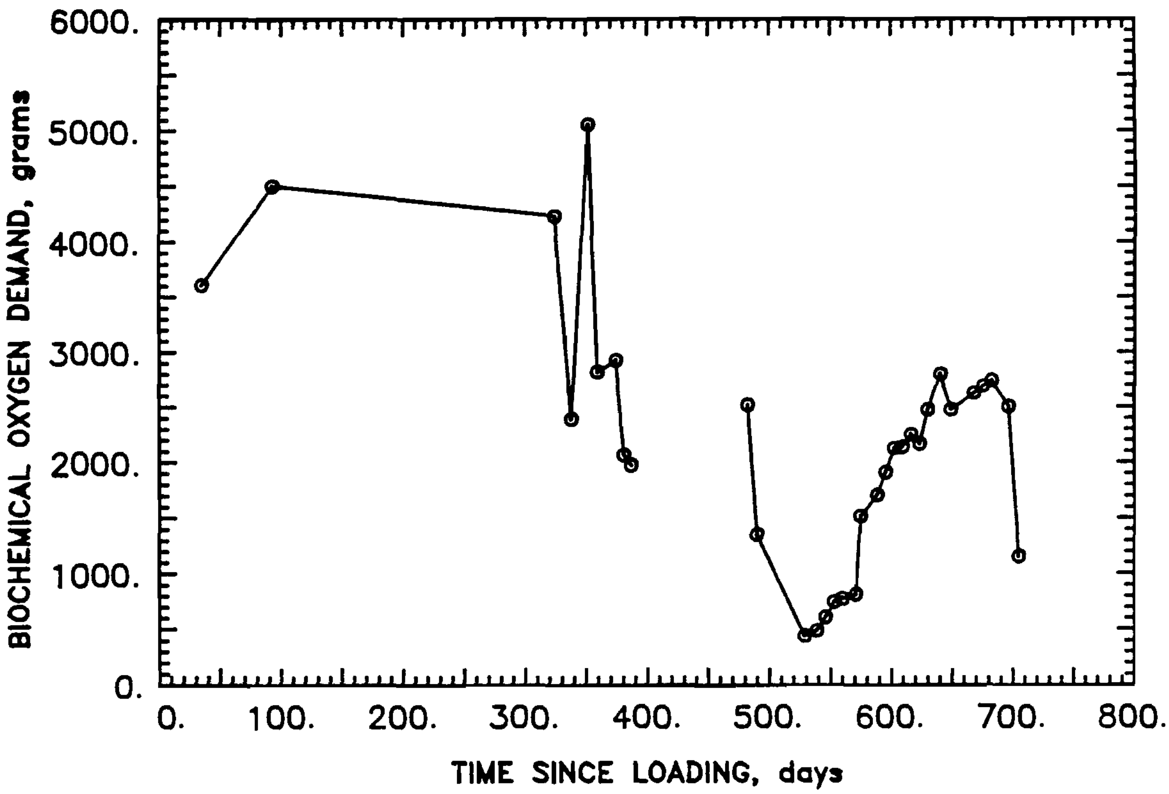


Figure 39. Biochemical Oxygen Demand of Column 4 Leachate

Changes in Aromatic Hydroxyl with Time--

The major aromatic hydroxyl (ArOH) constituents in leachate were assumed to be moderate to high molecular weight compounds similar if not identical to the humic substances commonly found in natural waters. These substances, derived from the decay of vegetation, are responsible for the yellow to brown colors characteristic of many surface waters. The chief sources of these substances in leachates include such materials as paper, sawdust, wood, leaves and other yard debris, and coffee grounds and vegetable food wastes. The ArOH compounds will be available both as directly soluble materials, which will be abundant during initial washout, and as products of hydrolysis and bacterial decomposition of source materials. The latter ArOH concentrations would be expected to vary in response to the chemical and biological environment established within the landfills as stabilization proceeds.

The variation of aromatic hydroxyl concentration and mass as a function of time is presented in Figures 40 through 43. Examination of these figures indicates that leachate ArOH levels for Columns 1 and 2 were very similar, with an initial rapid washout being followed by stabilization after approximately 150 days. This stabilization showed little indication of being influenced by the extended period of drought and cessation of leachate production. There was some indication that the stabilization was slightly retarded in Column 2, but the effect, if real, was slight. It was also observed that stable concentrations of ArOH in Columns 1 and 2 were very low, i.e., 10 to 20 mg/L, thereby indicating that the source materials for ArOH decomposed only very slowly to release humic-like substances into the leachate.

Columns 3 and 4 showed significantly different behavior upon comparison with Columns 1 and 2. The period of washout was substantially less pronounced than for Columns 1 and 2, with higher ArOH residuals remaining during the period between washout and cessation of leachate production. Therefore, it would appear that the higher levels of metal sludge contained in Columns 3 and 4 had a markedly inhibitory impact on any decomposition of ArOH in solution. This effect may have been due to direct inhibition of bacterial activity by the toxic metals transferred from the sludge to the leachate, or by an interaction between the ArOH and the heavy metals which may have acted to reduce the susceptibility of these compounds to degradation.

Using the same relative chronological description as before, the experimental phases observed for ArOH are listed in Table 19, and the corresponding average concentrations and masses of ArOH in the leachates during these phases are shown in Figure 44. Upon examination of the data for Columns 1 and 2 and Columns 3 and 4, an especially interesting effect of leachate recycle became clearly evident. It would have been expected that the leachate ArOH levels during washout would have been either essentially the same for all four columns or higher for those columns carrying the greater quantities of toxic or inhibitory sludges. Instead, the ArOH levels in the leachate decreased smoothly with increasing loadings of sludge in the columns. The decrease in ArOH during washout was about 66 percent from Column 1 to Column 4. This behavior was probably a consequence of a chemical or sorptive interaction between the humic materials and heavy metals in the sludge, with the resulting fixation of a portion of the ArOH on the solid phase metal

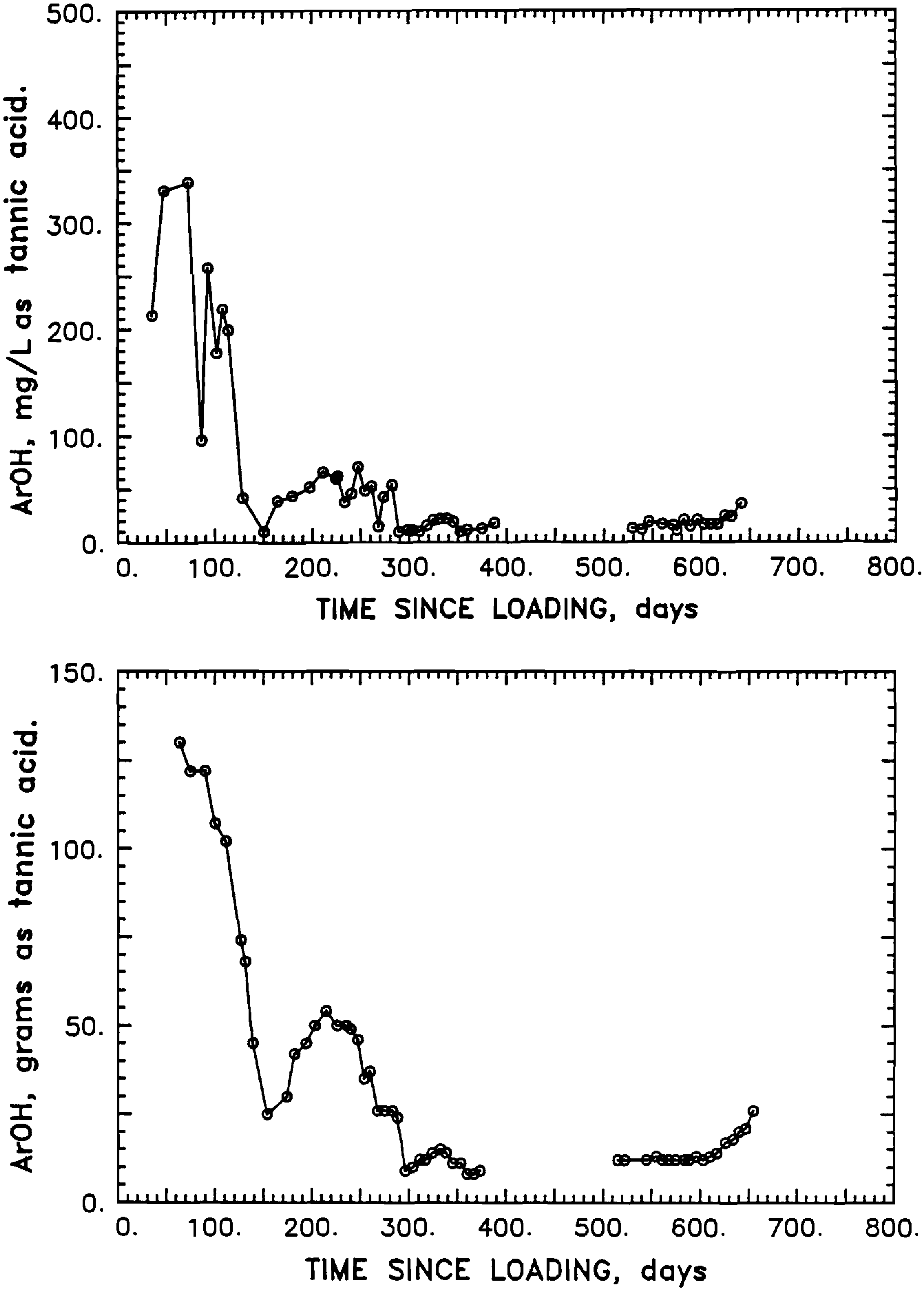


Figure 40. Aromatic Hydroxyl Content of Column 1 Leachate

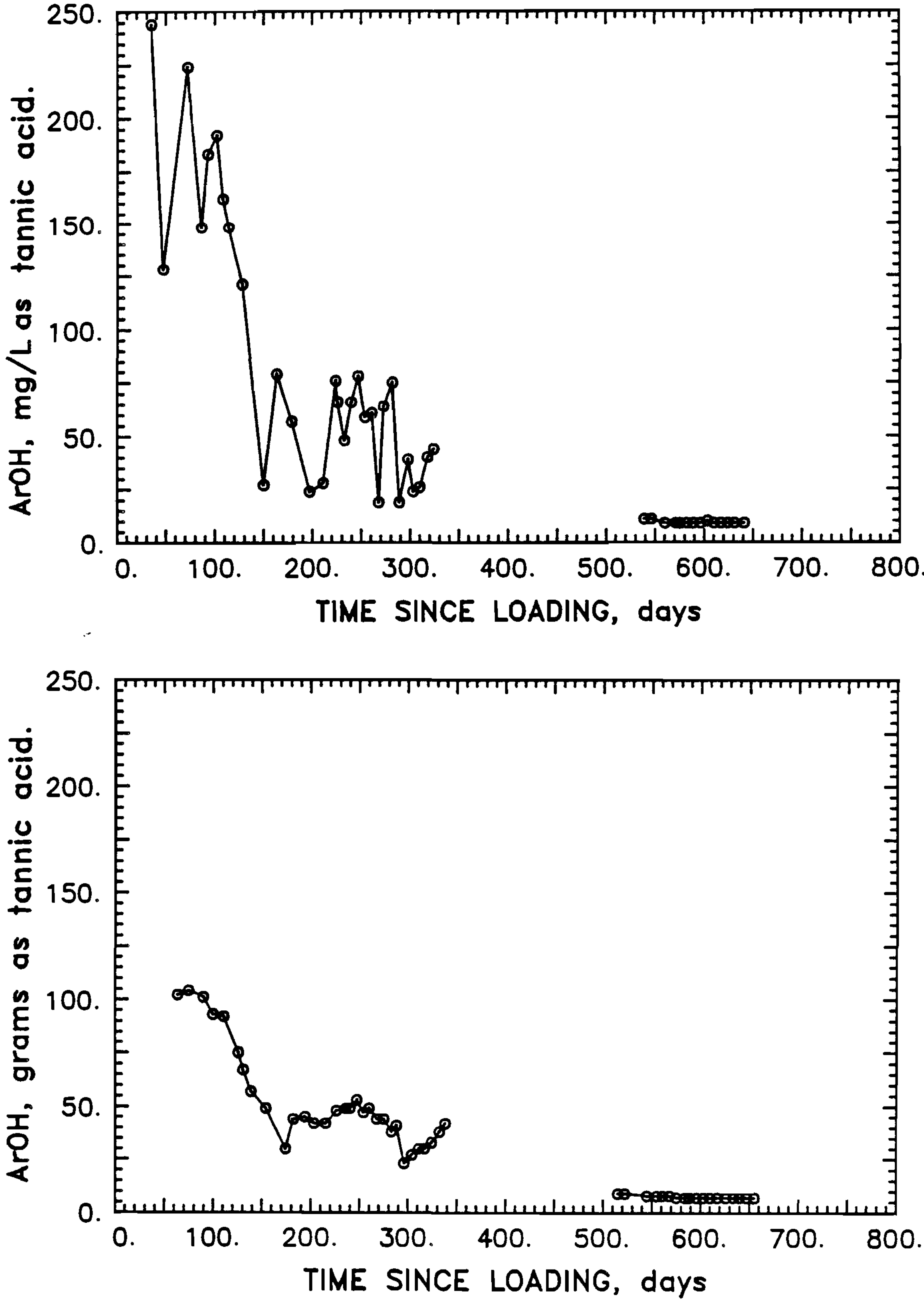


Figure 41. Aromatic Hydroxyl Content of Column 2 Leachate

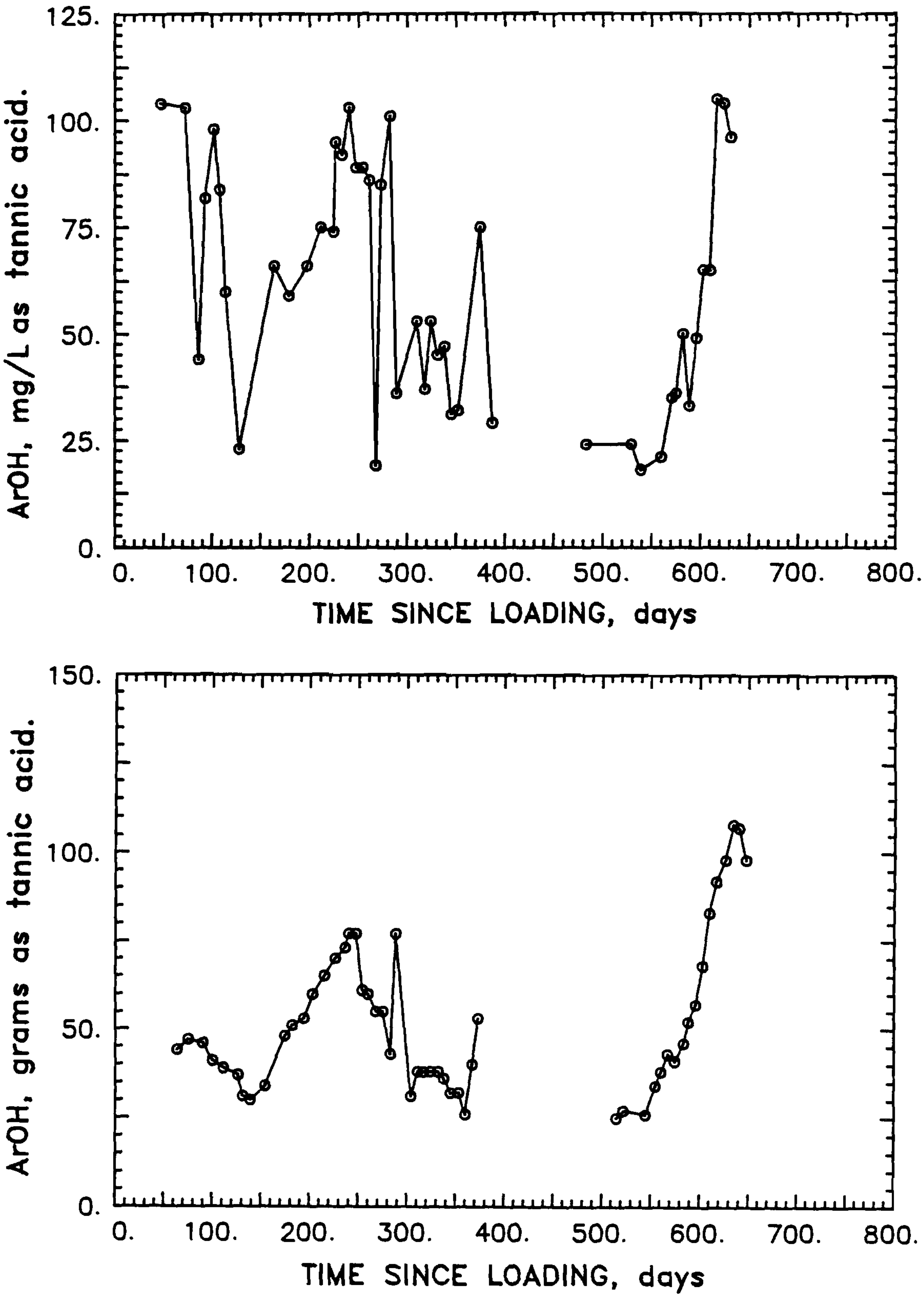


Figure 42. Aromatic Hydroxyl Content of Column 3 Leachate

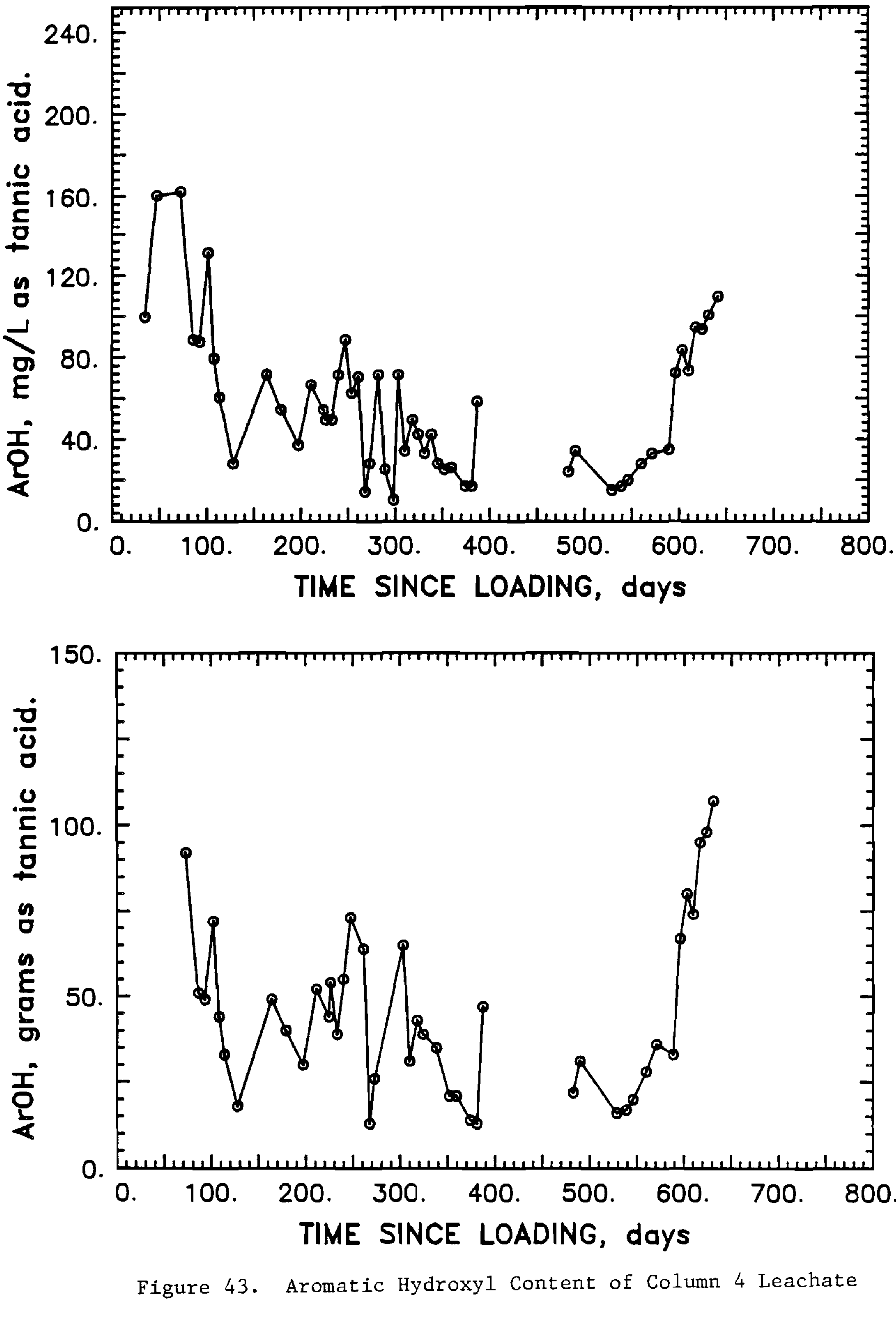


Figure 43. Aromatic Hydroxyl Content of Column 4 Leachate

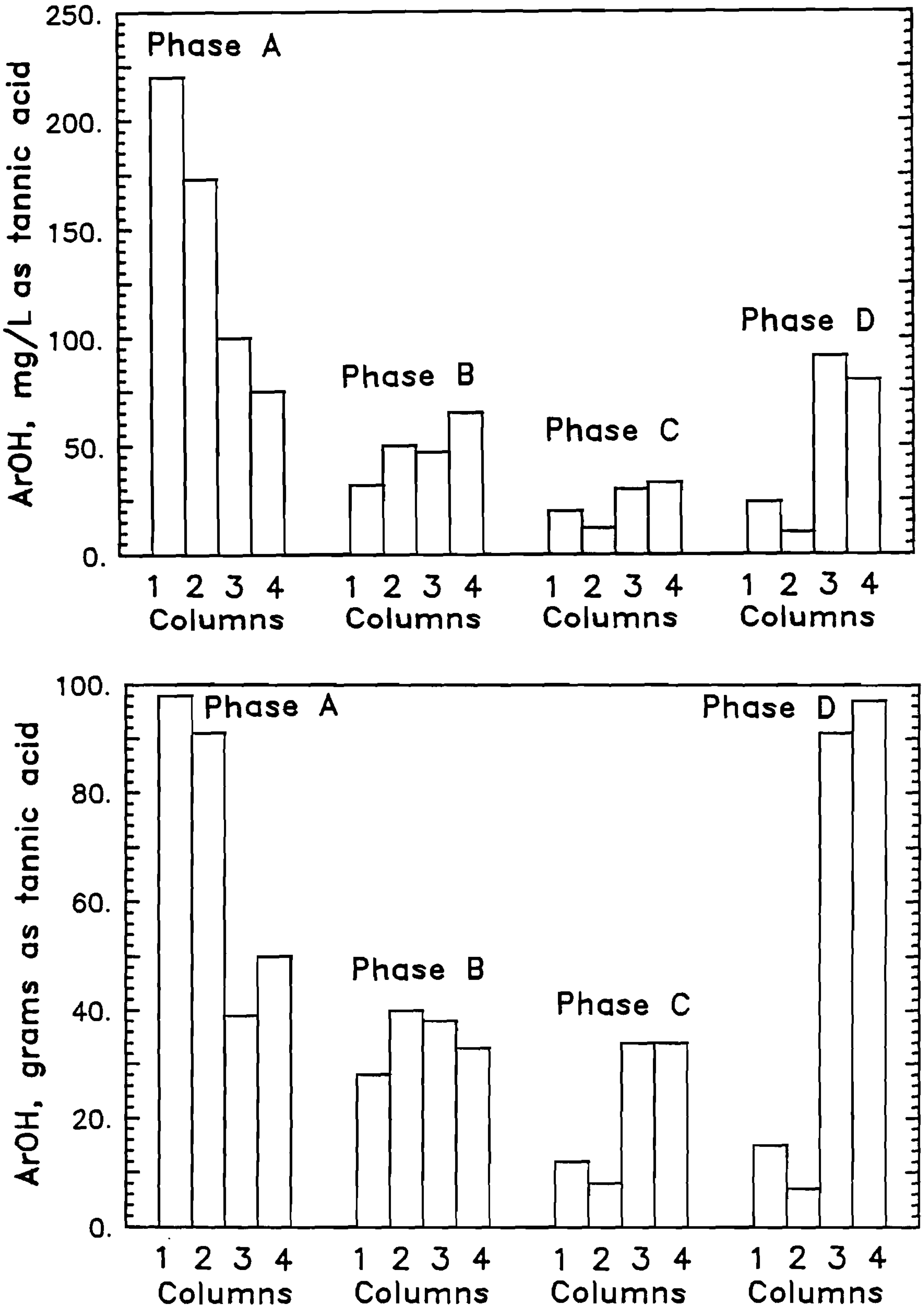


Figure 44. Average Content of Aromatic Hydroxyl During Experimental Phases

TABLE 19. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR AROMATIC HYDROXYL ANALYSES

Experimental Phase	Days	Operational Characteristics
A	0-150	Washout
B	150-380	Initial stabilization
C	480-600	Post-drought
D	600-650	Terminal

hydroxides. The increased contact between the leachate and the solid phase materials arising from leachate recycle will certainly have facilitated this ArOH fixation process.

The sharp increase in leachate ArOH levels from Columns 3 and 4 during the later stages of column operation suggests a combination of inhibition of biological decomposition of the ArOH and the possible displacement of material bound to the metal sludge by sulfides (Equation 2).

$$M(ArOH)(s) + S^{-2} \rightleftarrows MS(s) + ArOH \qquad \ldots(2)$$

where; M(ArOH)(s) is a solid phase metal-humic complex, S^{-2} is sulfide, MS(s) is solid metal hydroxide and ArOH is soluble humic substance.

Changes in Carbohydrates with Time--

There are several sources of soluble carbohydrates in domestic refuse. The primary source of readily soluble carbohydrates in these landfill systems will be simple sugars discarded as part of household wastes. The sugars, mainly sucrose, will wash out rapidly and be highly accessible as substrates and, in the absence of inhibition, should be metabolized very rapidly and completely by microbiological activity.

In addition to these sources of readily soluble carbohydrates, refuse contains an abundant reservoir of complex carbohydrates, not directly soluble in themselves, but capable of hydrolytic conversion to simpler sugars and eventually to glucose by microbial activity. These complex carbohydrates are mainly cellulose in the form of paper, wood, sawdust, etc., and starch. (Some confirmation of the significance of cellulose as a source of low molecular weight carbohydrates in the leachates of these investigations was the observation that the leachates had substantial numbers of cellulose hydrolyzing anaerobes of the genus *Clostridium* (Bender, 1983, 1984) which are capable of converting cellulose to glucose.)

The variation of carbohydrate concentrations and masses over time is shown in Figures 45 through 48. As was the case for the aromatic hydroxyl levels, the data from the four columns can be separated into pairs. For Columns 1 and 2, an intital washout occurred and, although these columns were generally similar in behavior over the first 250 days, Column 2 showed a marked increase in leachate carbohydrate level immediately prior to cessation of leachate production. This increase is difficult to rationalize, since it was not consistent with variations in other organic parameters, including carbohydrate levels from the other columns. However, since the carbohydrate levels as measured were subject to a high degree of variability, it was possible that this dramatic increase in carbohydrate concentration represented simple sampling/analytical scatter.

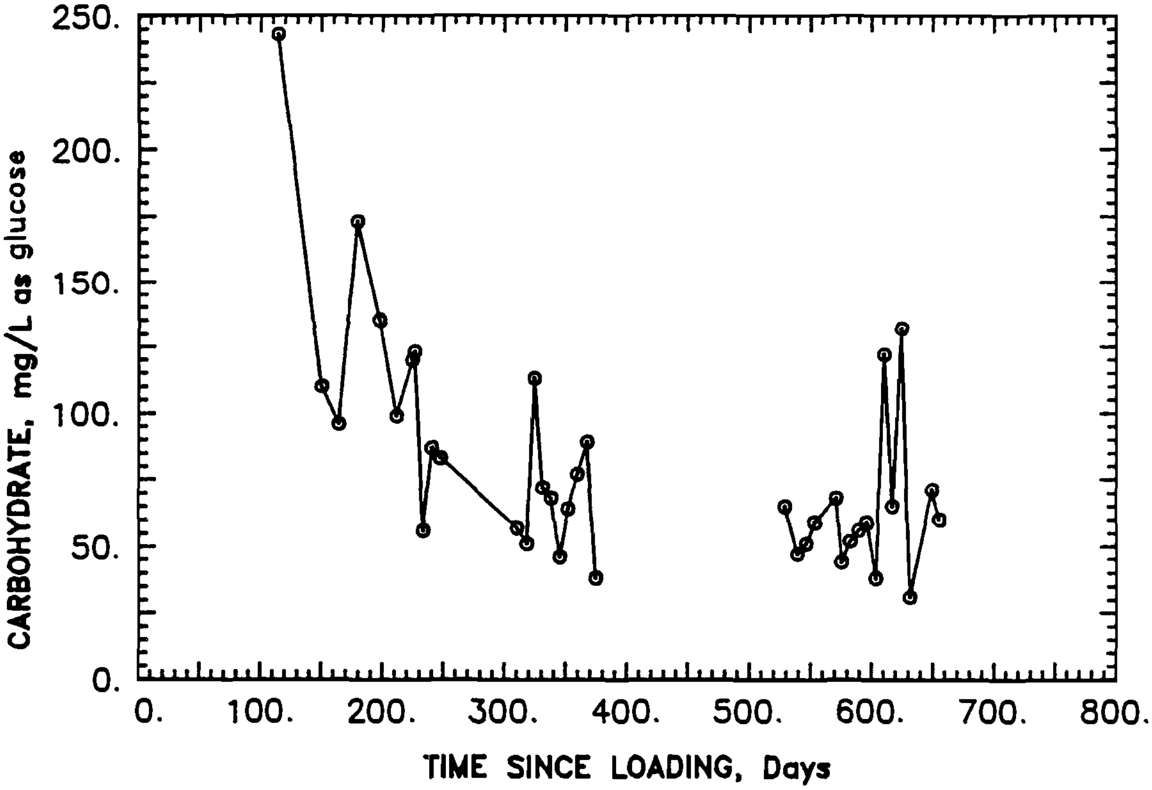
The leachate carbohydrate data from Columns 3 and 4 were quite similar yet substantially different from those of Columns 1 and 2. The inhibitory impact of the metal sludges on the balance between carbohydrate generation and consumption is clearly evident for these latter columns. There was no detectable trend in carbohydrate levels with respect to the initial washout values in the 380+ days prior to cessation of leachate generation. Since the probability of a precise balance between production and consumption of carbohydrates being maintained in both Columns 3 and 4 over this period was very low, the more likely explanation for this lack of a clear trend is a nearly complete heavy metal inhibition of both carbohydrate generation and consumption. The consequence of such a complete inhibition would be the maintenance of leachate carbohydrates at levels approximating the initial washout values as was the case for Columns 3 and 4.

During the first 120 days following resumption of leachate generation, the leachate carbohydrate concentrations for Columns 3 and 4 were slightly depressed with respect to the early phases of the experimental period. It is probable that the prolonged period without leachate recycle and resulting intimate contact of leachate with metal sludges provided an opportunity for limited carbohydrate consumption by microorganisms. However, carbohydrate levels recovered to a pattern similar to that observed during the early phases of column operation after this 120-day period. This pattern was then maintained for the remaining period of column operation.

The experimental phases observed for carbohydrates are listed in Table 20 and the average values of concentration and mass for these phases are shown in Figure 49. The bar graphs shown in this figure clearly illustrate the trends described in the preceding section. Again, it is evident that quantities of toxic sludges in Column 2 had little impact on the quality of leachate generated in the recycle mode when compared with Column 1. Clearly, however, the increase in sludge quantity between Columns 2 and 3 was sufficient to exceed the capacity of the system to overcome heavy metal toxicity. Consequently, the data for Columns 3 and 4 showed strong evidence of toxic or inhibitory effects.

Changes in Total Volatile Acids and Carboxylic Acids With Time--

The origins of the members of this group of compounds are as varied as the components of the group. Aliphatic acids of high molecular weight will derive from the hydrolysis of fats and oils and dissolution of natural soaps



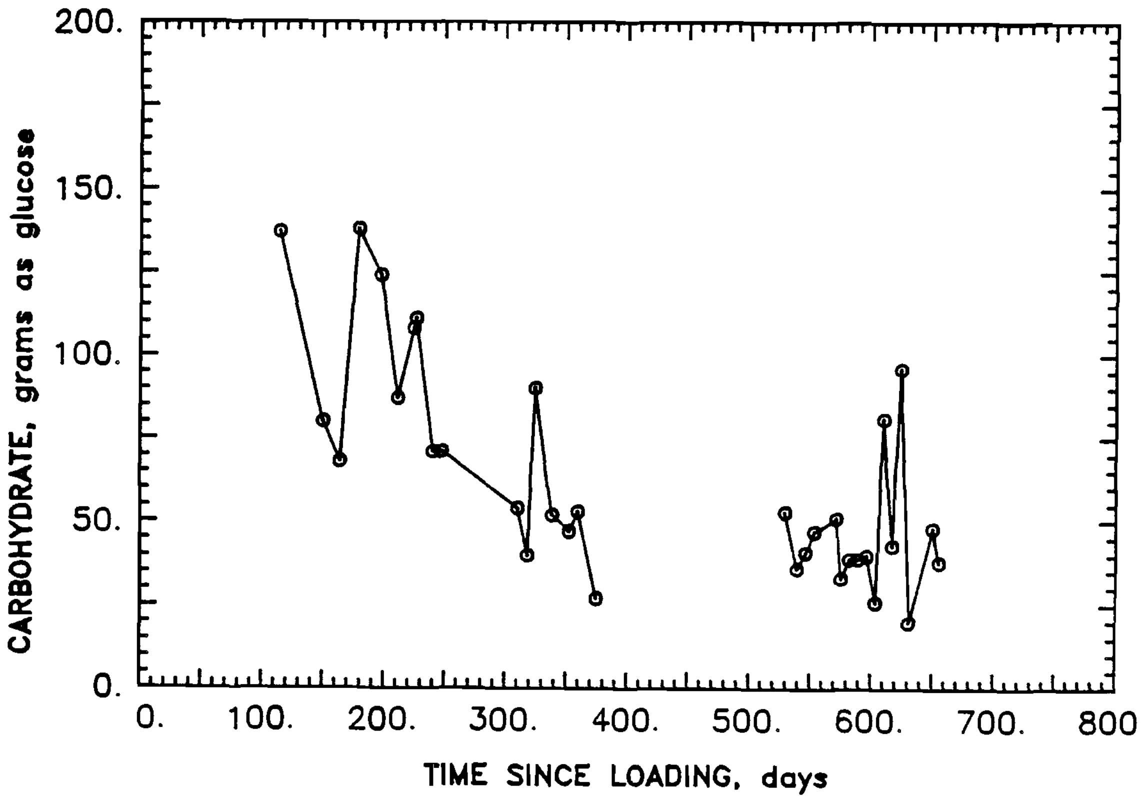
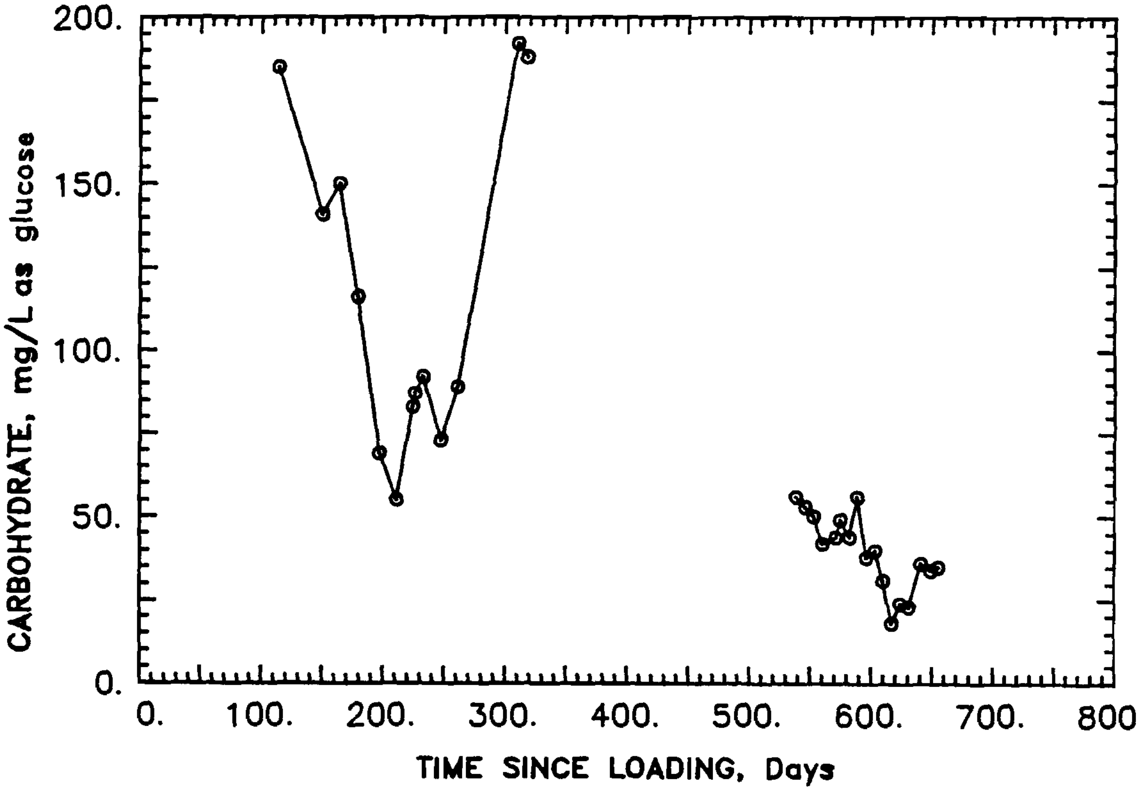


Figure 45. Carbohydrate Content of Column 1 Leachate



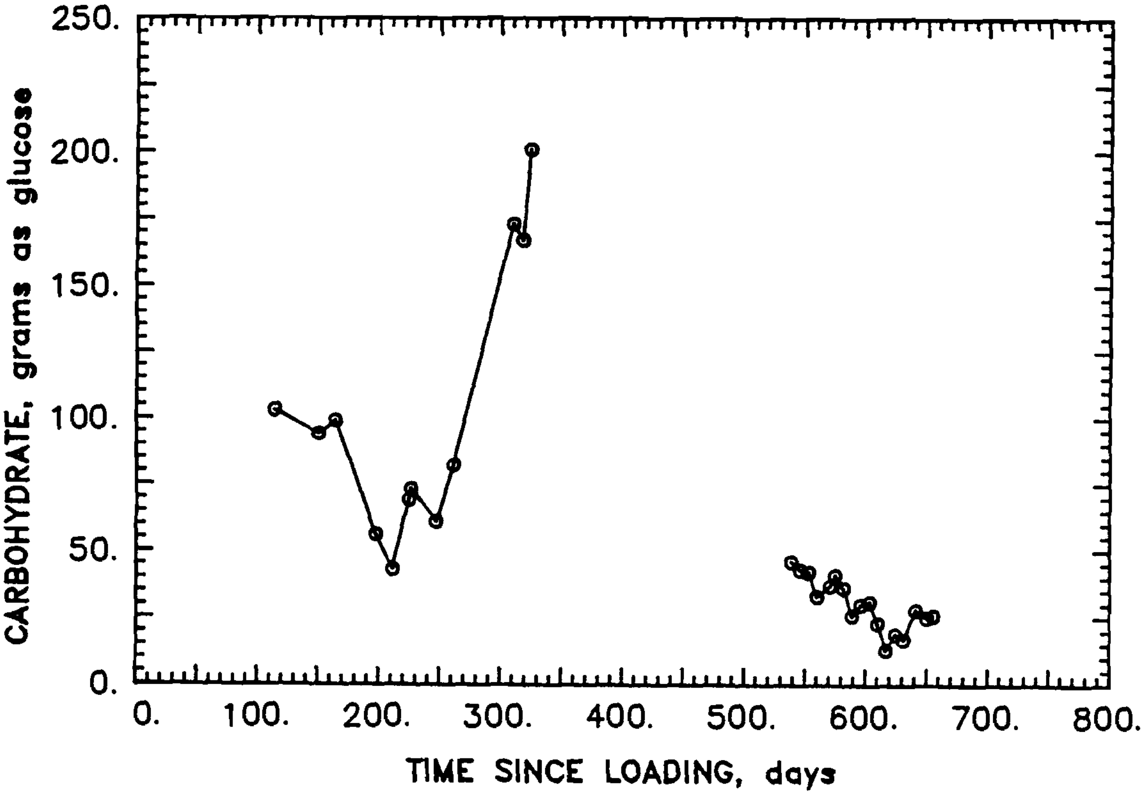


Figure 46. Carbohydrate Content of Column 2 Leachate

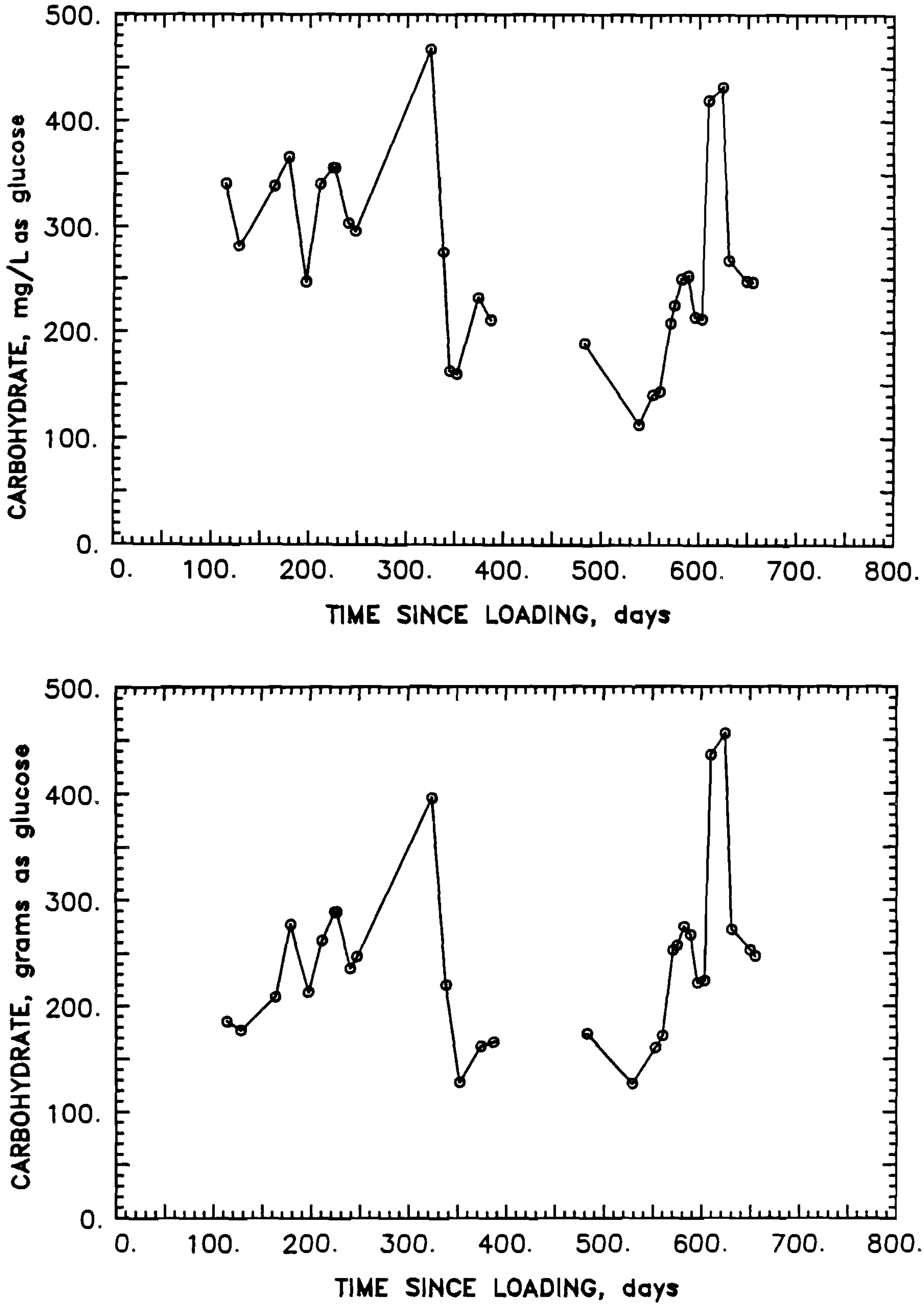


Figure 47. Carbohydrate Content of Column 3 Leachate

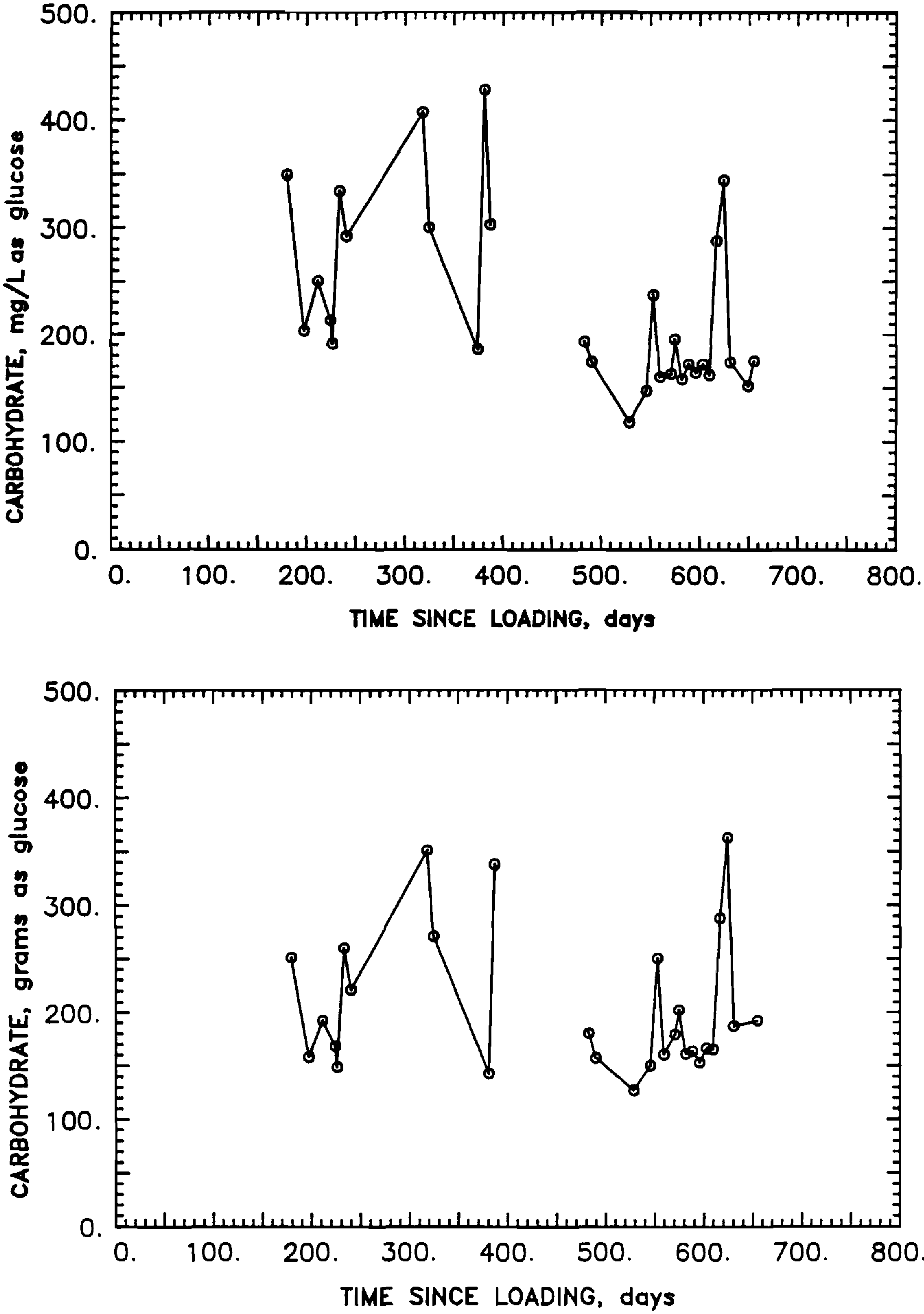
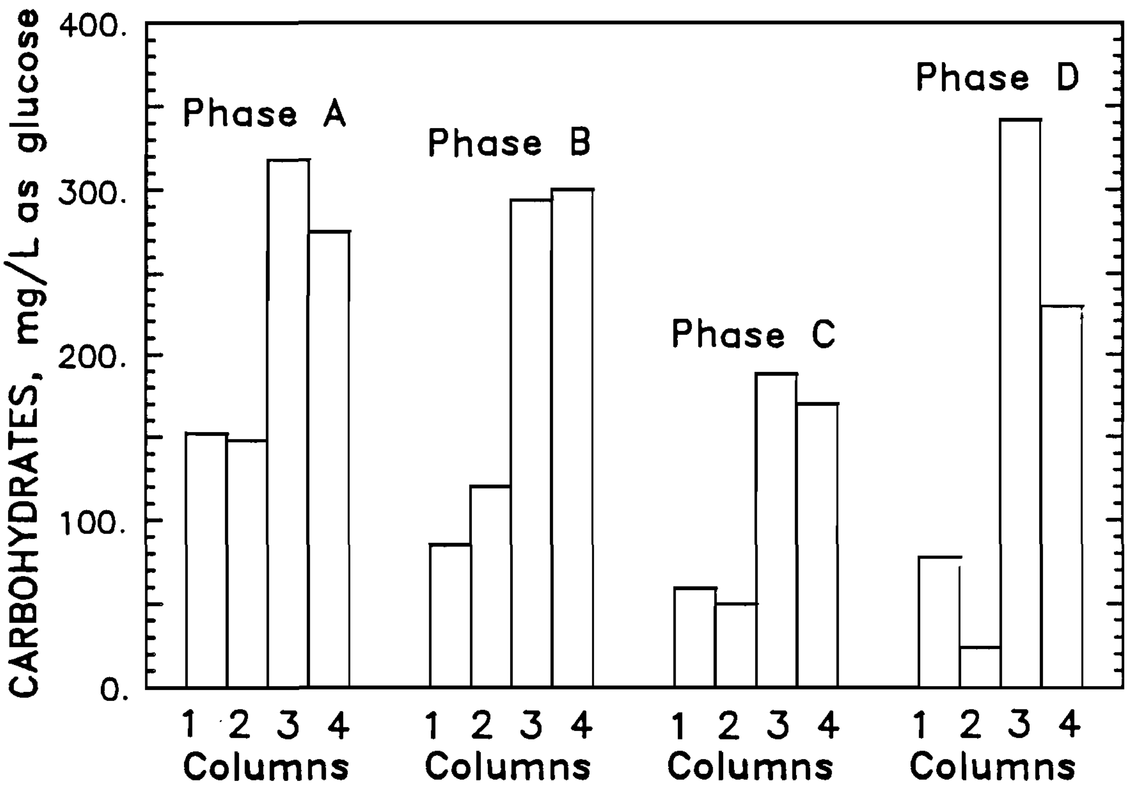


Figure 48. Carbohydrate Content of Column 4 Leachate



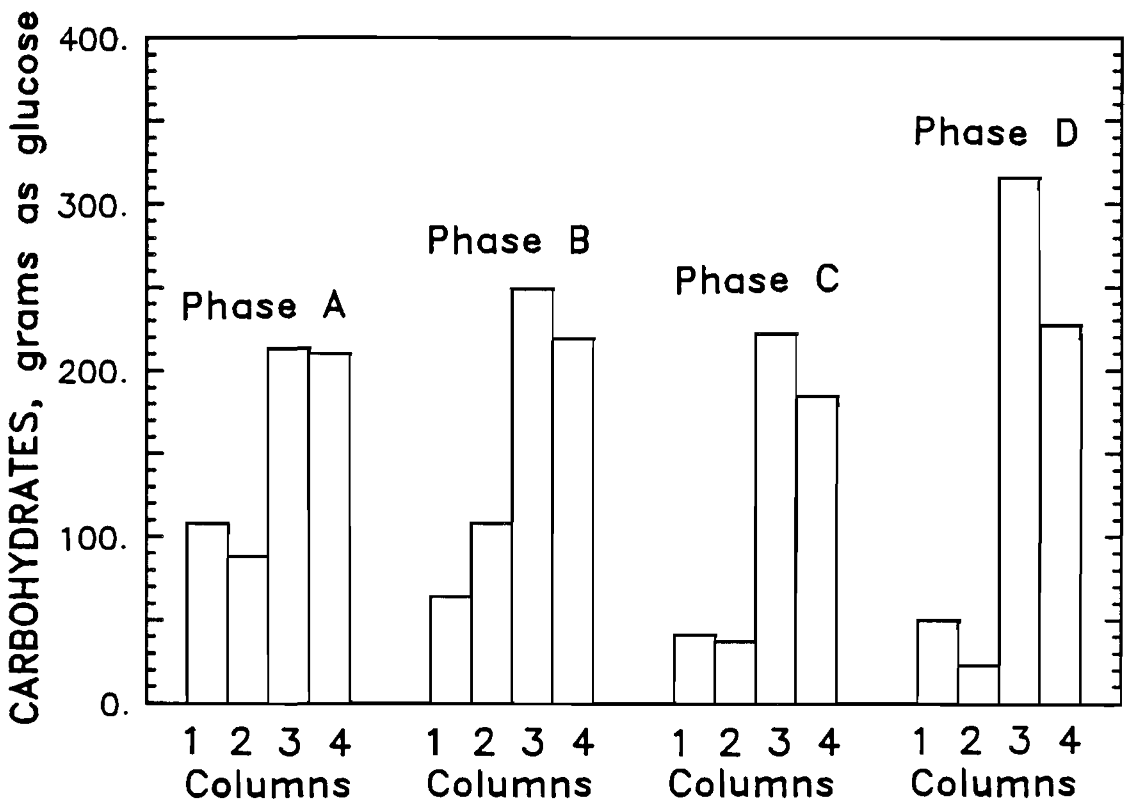


Figure 49. Average Content of Carbohydrates During Experimental Phases

TABLE 20. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR CARBOHYDRATE ANALYSES

Experimental Phase	Days	Operational Characteristics
A	0-150	Washout
B	150-380	Stabilization
C	480-600	Post-drought
D	600-670	Terminal

in domestic refuse. Bacterial activity can convert these acids with the formation of acids of lower molecular weight, generally included in the total volatile acid (TVA) group having between two and five carbon atoms. In addition, the normal processes of anaerobic acid formation from organic substrates will provide abundant volatile aliphatic acids. Aromatic acids will derive mainly from the decomposition of plant lignans and humic substances as well as washout of soluble aromatic acids from the same source materials.

Although logic would dictate that the carboxylic acid concentrations equal or exceed the concentration of TVA in all cases, the actual data displayed an erratic relationship between the two groups of analyses. In approximately 50 percent of the cases, the TVA concentration was greater than the carboxylic acid concentration. Scrutiny of this anomoly indicated that the primary cause of this problem was the colorimetric analysis for carboxylic acids rather than the much more specific gas chromatographic analysis used for the determination of volatile acids. Therefore, it was necessary to weigh the carboxylic acid data within this perspective of analytical uncertainty and rely more on the specific TVA analyses.

The variations in total volatile acid concentrations and masses as a function of time are shown in Figures 50 through 53. A clear trend is apparent in the leachate data obtained for Column 1 through Column 4. The leachate from Column 1 showed a rapid decrease from high initial levels of TVA to a stable level immediately prior to the drought-induced cessation of leachate production. This stable level of TVA was re-established at once upon the resumption of leachate formation and continued unchanged until the termination of the project period. The overall process of rapid volatile acid generation and consumption followed by establishment of a stable level of leachate TVA occurred smoothly and uneventfully for the heavy metal-free column.

Data from Column 2 had characteristics which were intermediate in nature with respect to the transition from those of Column 1 to Column 3. The initial rapid decrease in leachate TVA levels was very similar to that observed for Column 1, but was followed by a rapid increase in levels

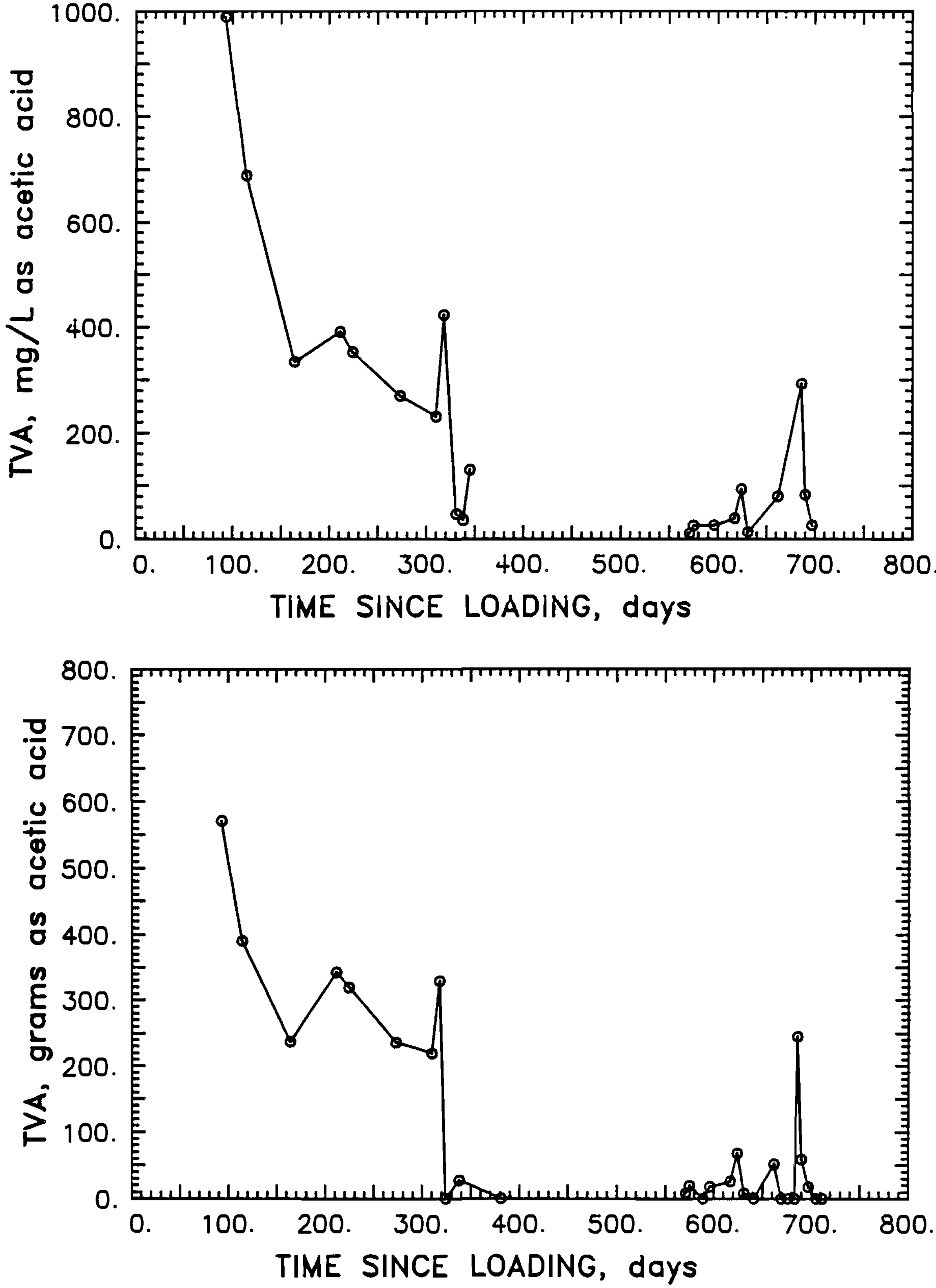


Figure 50. Total Volatile Acid Content of Column 1 Leachate

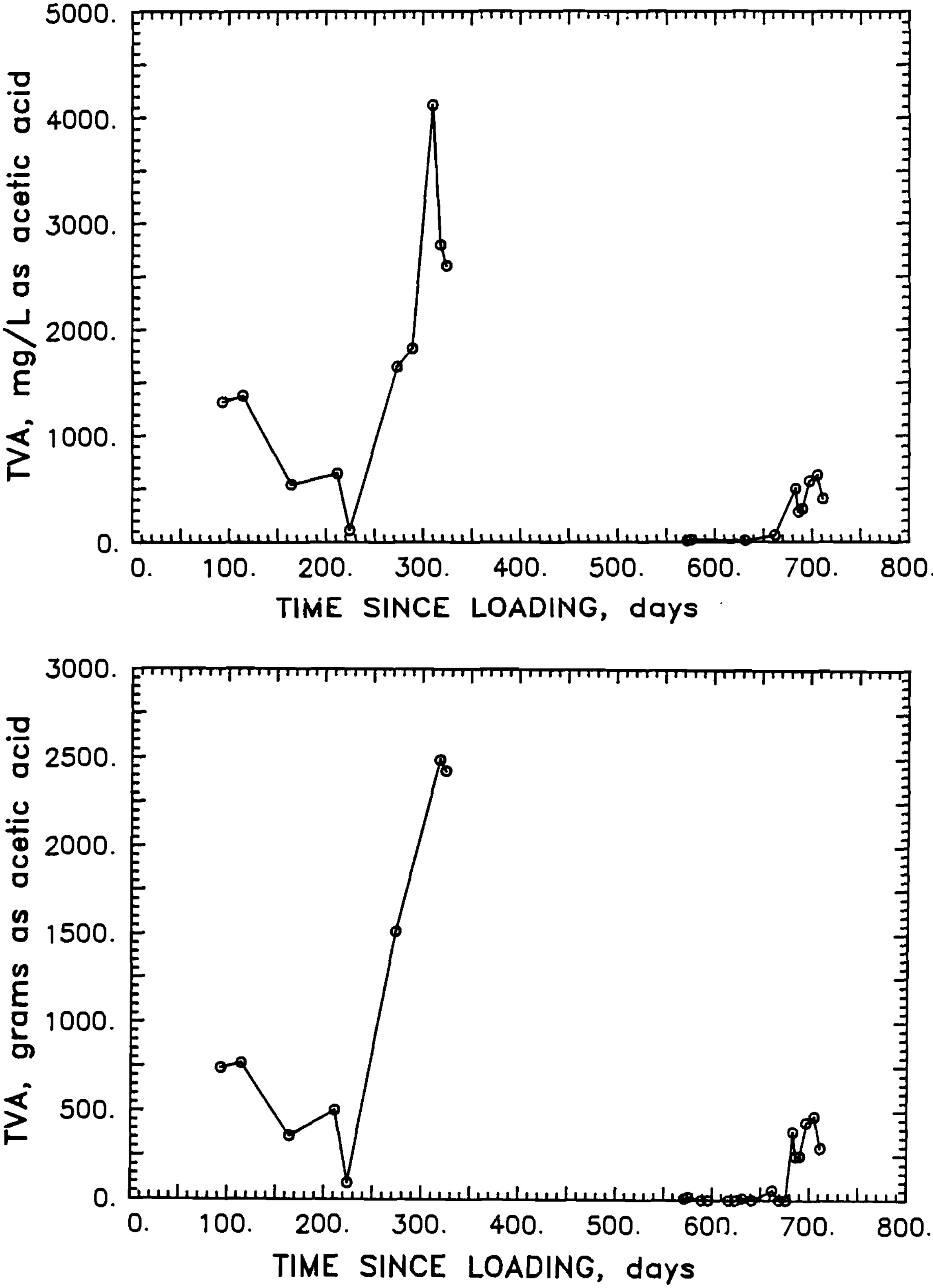


Figure 51. Total Volatile Acid Content of Column 2 Leachate

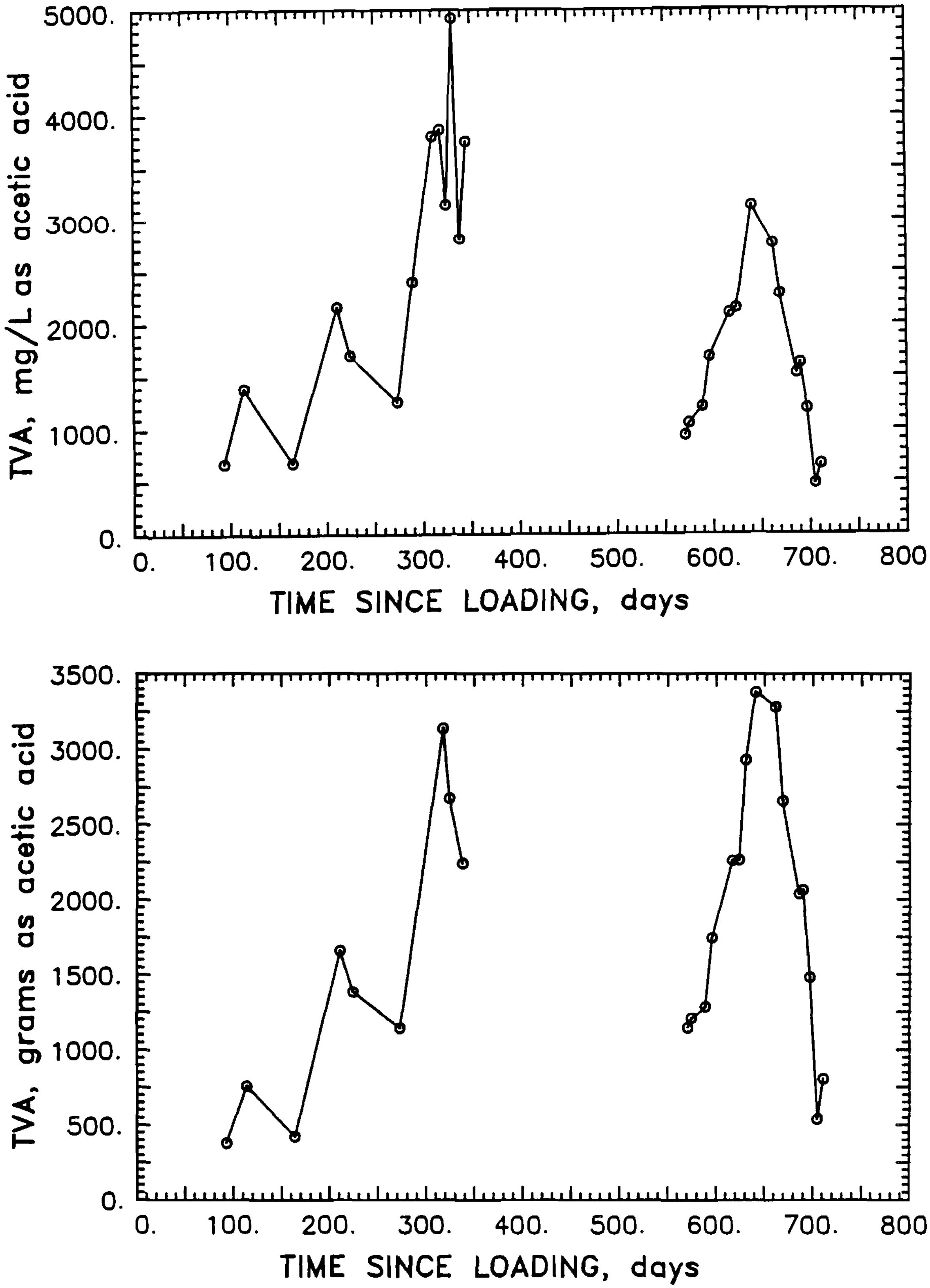


Figure 52. Total Volatile Acid Content of Column 3 Leachate

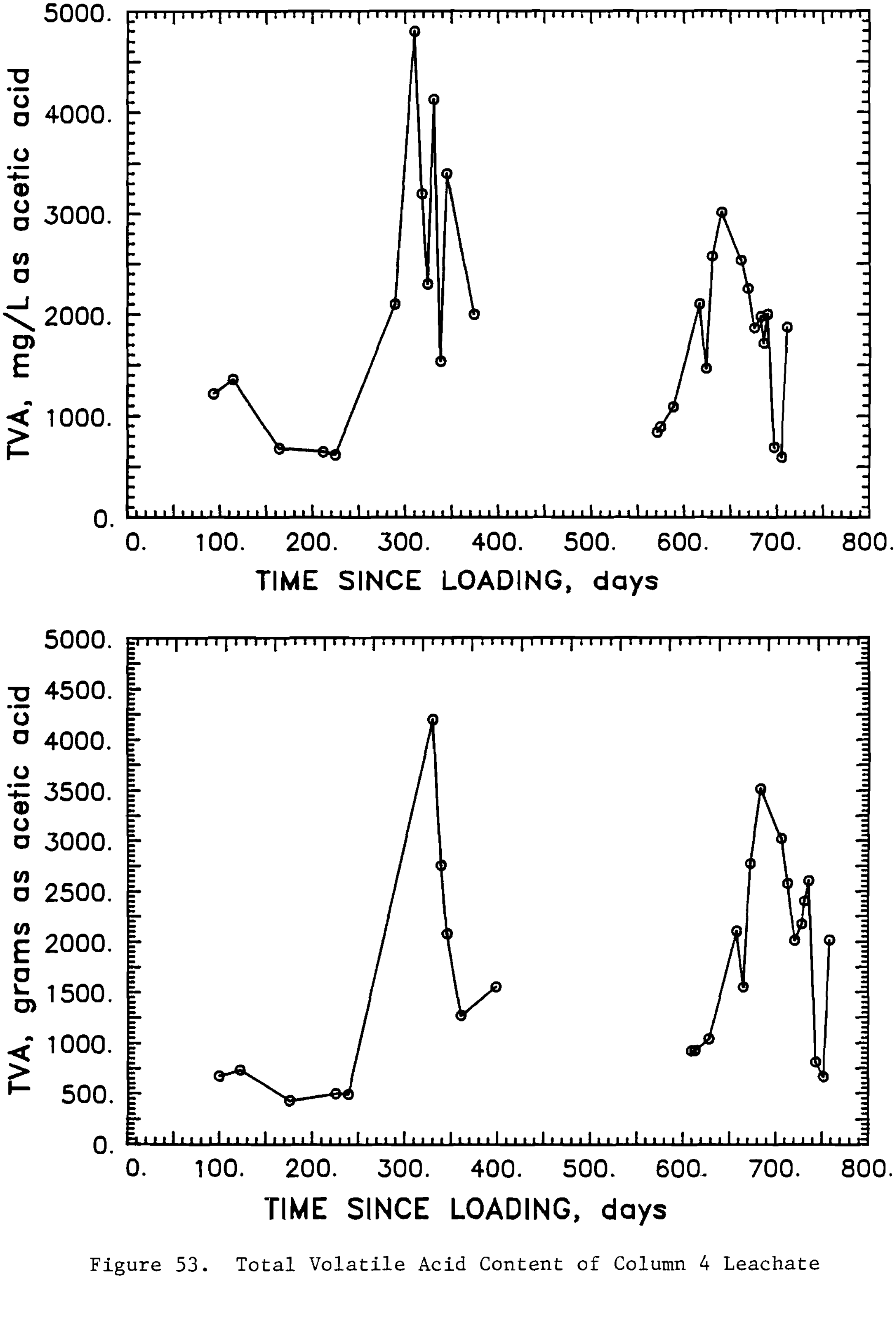


Figure 53. Total Volatile Acid Content of Column 4 Leachate

immediately prior to the cessation of leachate generation. Upon resumption of leachate production, the TVA levels in the leachate from Column 2 were very similar to those during the equivalent period for Column 1. However, between 650 days and the termination of operations at 760 days, a slight but definite trend toward increasing leachate TVA concentrations became evident. This behavior suggested development of a cyclic inhibition of acid consumption by the heavy metal sludge in the simulated landfill.

Columns 3 and 4 were virtually indistinguishable from each other with respect to trends in leachate TVA levels with time. For both columns, the initial volatile acid levels, rather than decreasing as in Columns 1 and 2, increased more or less steadily up to approximately Day 300, followed by a substantial decrease up to the cessation of leachate production. During the period following resumption of leachate production, TVA values were virtually identical in the leachates from both columns. The TVA values, which had decreased to levels similar to those present during the early stages of the studies, increased rapidly to a peak approximately 70 days after resumption of leachate production. During the remaining 70 days of operation, the TVA level decreased to a value similar to the level at which it started at Day 570. The quantitative and qualitative similarities between the behavior of Columns 3 and 4 during this period were striking as was the symmetry of the concentration versus time curves. The suggestion of a cyclic inhibition of volatile acid consumption, while not unequivocally established, was again quite strong.

The virtually identical behavior of Columns 3 and 4 in terms of leachate TVA concentrations was consistent with results obtained for the other organic parameters studied. It appears that, while these simulated landfill systems were able to accommodate the toxic loadings of Column 2 with only limited evidence of inhibition or toxicity, the sludge loadings in Columns 3 and 4 were sufficient to overwhelm the assimilative capacity of the landfill columns for the metal sludge, thereby imposing toxicity on the inherent processes of stabilization.

Bearing in mind the apparent problems associated with the carboxyl group analysis, the trends observed in the concentrations for this parameter shown in Figures 54 through 57 were, on the whole, remarkably similar to the trends observed for the total volatile acids. Beyond this very general observation, more detailed conclusions regarding this parameter were not logical.

The production phases observed for total volatile acids are listed in Table 21 and illustrated in Figure 58. These data reinforce the trends discussed in the previous section. The similarity between Columns 3 and 4 is obvious, while the transitional nature of Column 2 is also clearly apparent. Moreover, the overall inhibitory impact of the metal sludge was evident in Column 2 in which some inhibition of volatile acid consumption occurred, whereas it was complete for Columns 3 and 4.

Changes in Total Inorganic Carbon with Time--

The behavior of total inorganic carbon (Figures 59 through 62) suggested the probable beneficial impact of leachate recycle in systems containing heavy metal/lime (CaO) sludges. An examination of these figures indicates the

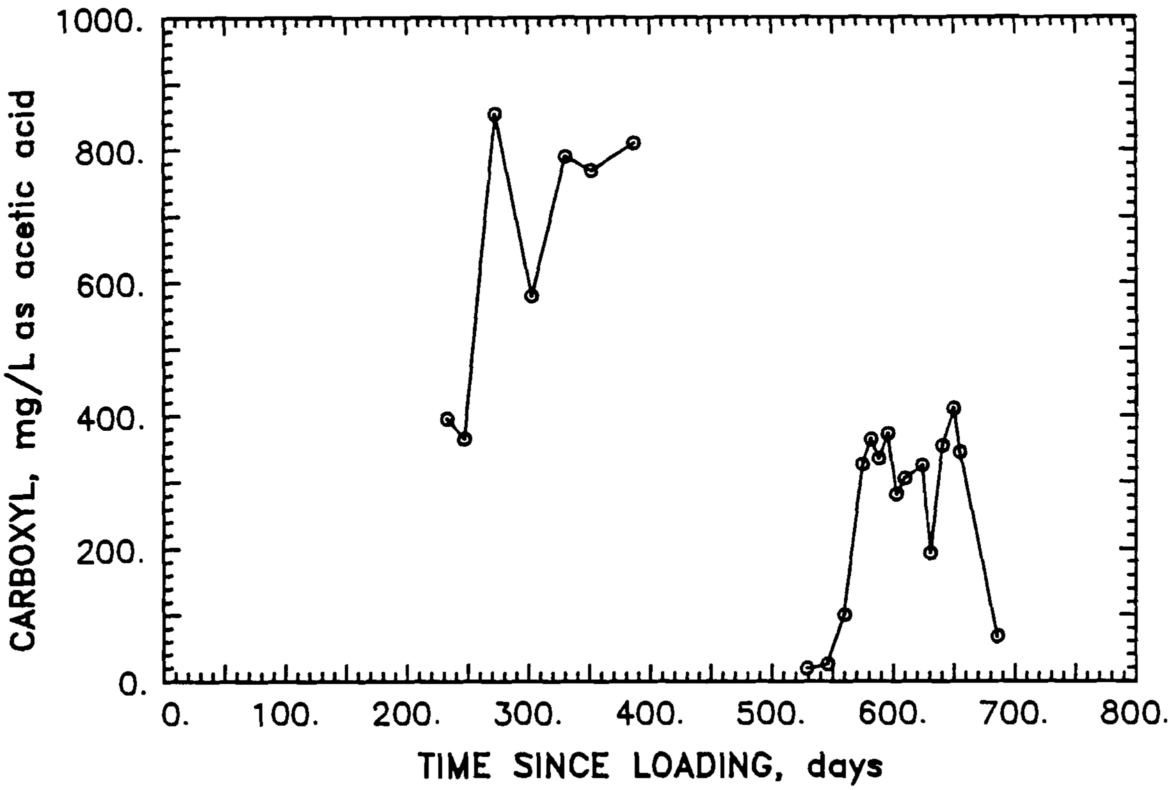


Figure 54. Carboxyl Content of Column 1 Leachate

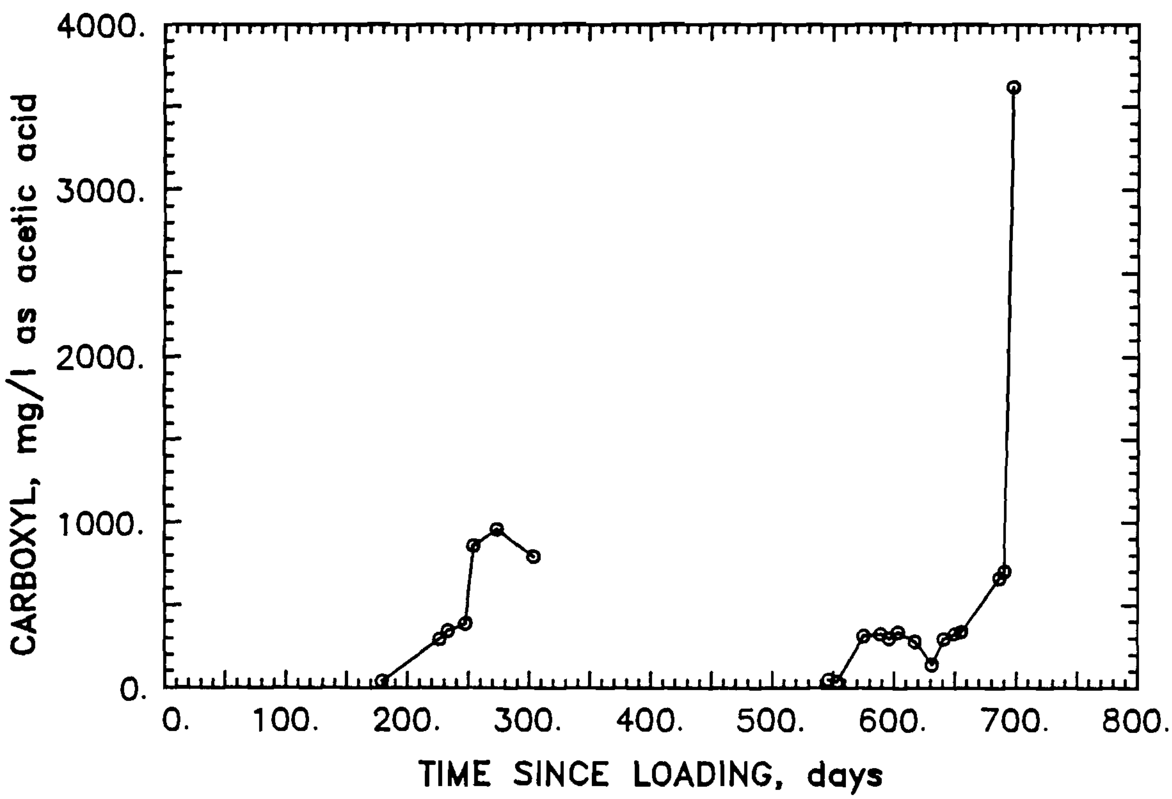


Figure 55. Carboxyl Content of Column 2 Leachate

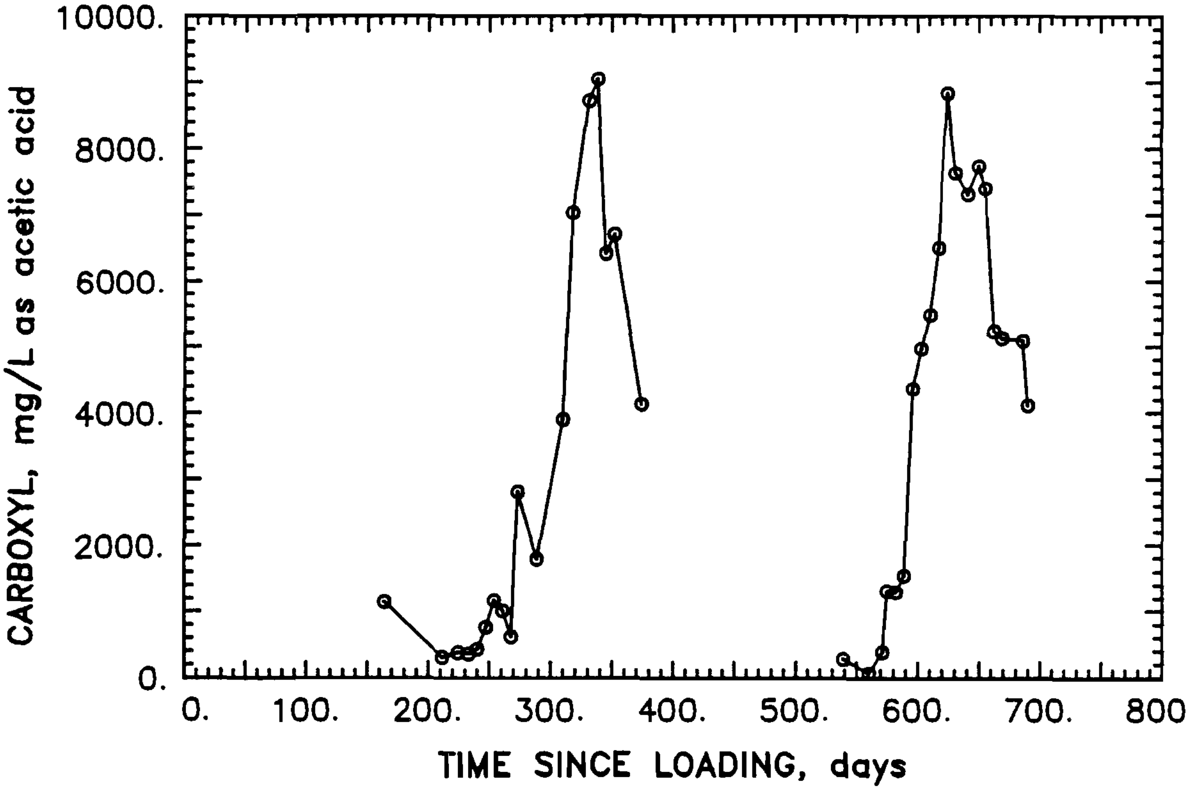


Figure 56. Carboxyl Content of Column 3 Leachate

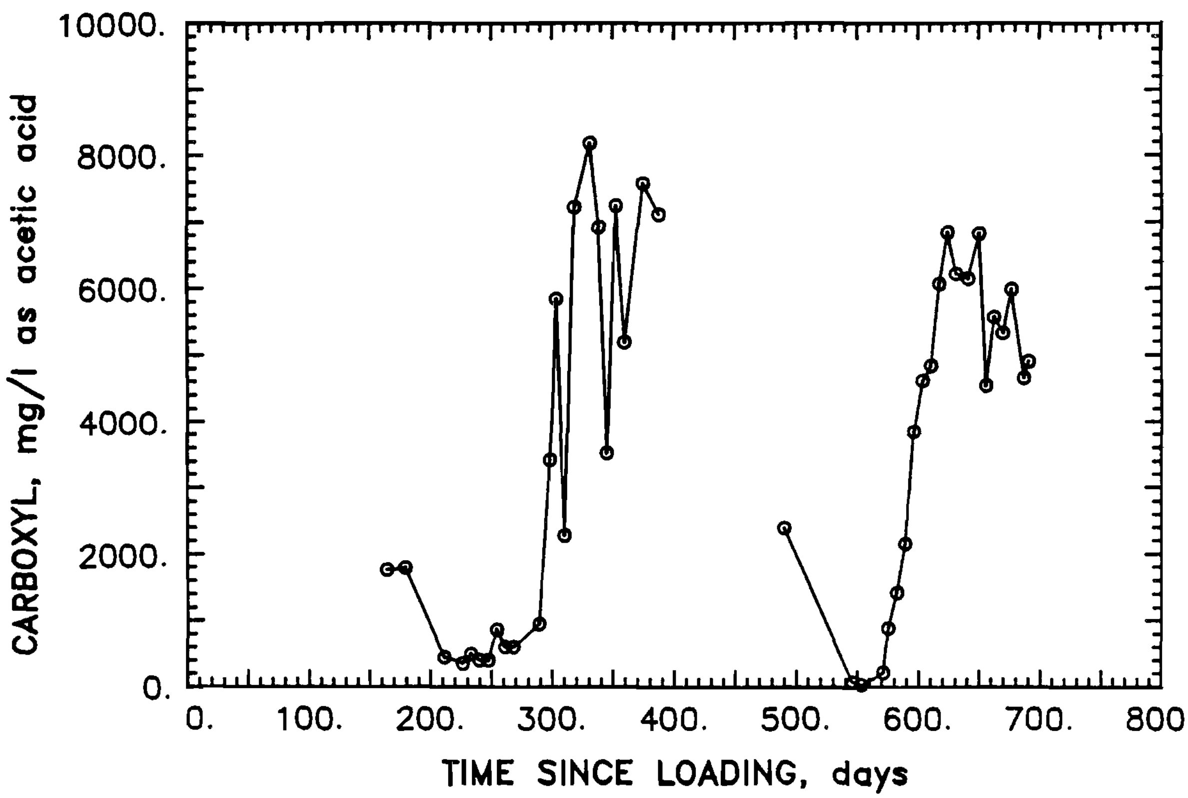


Figure 57. Carboxyl Content of Column 4 Leachate

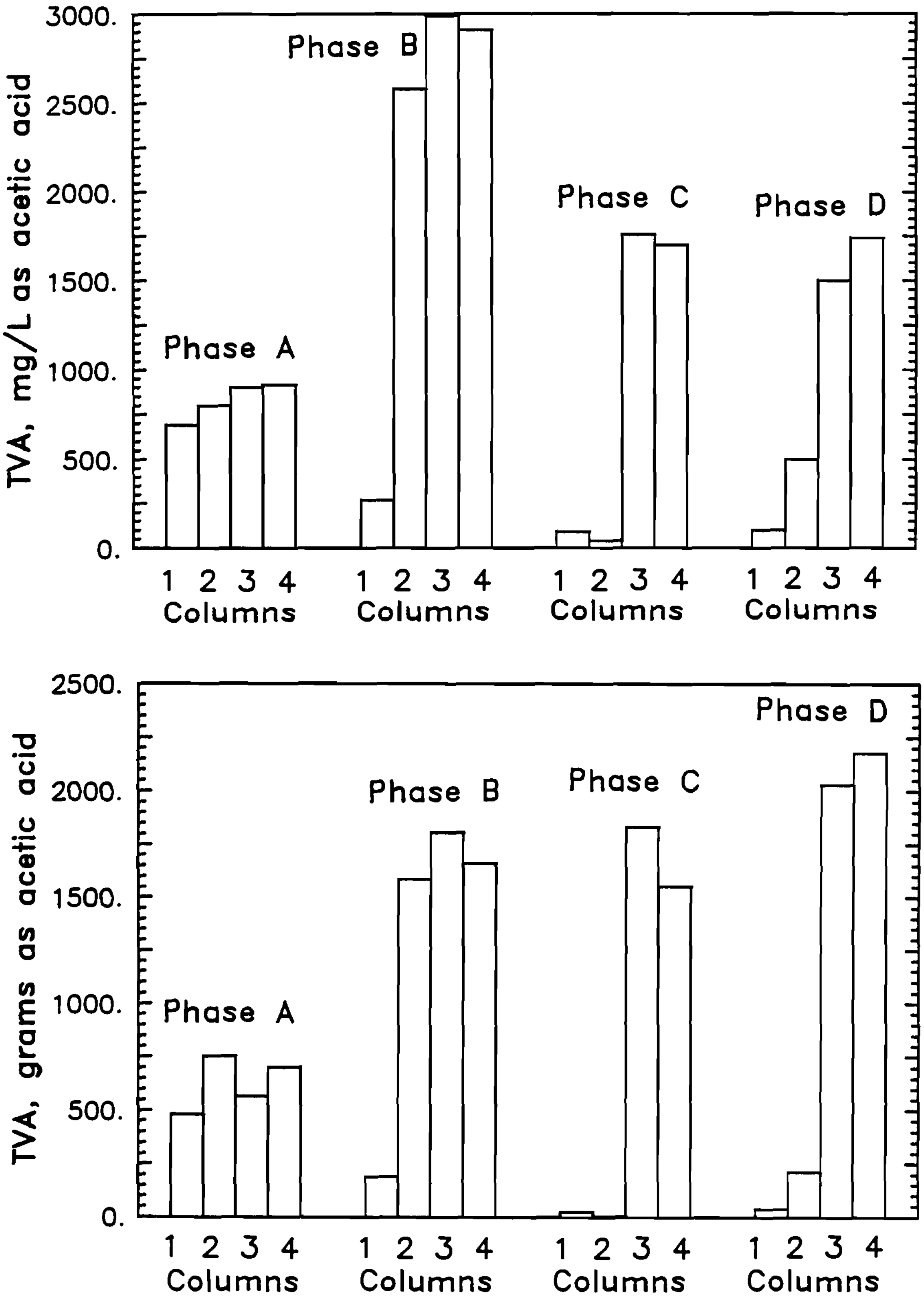


Figure 58. Average Content of Total Volatile Acids During Experimental Phases

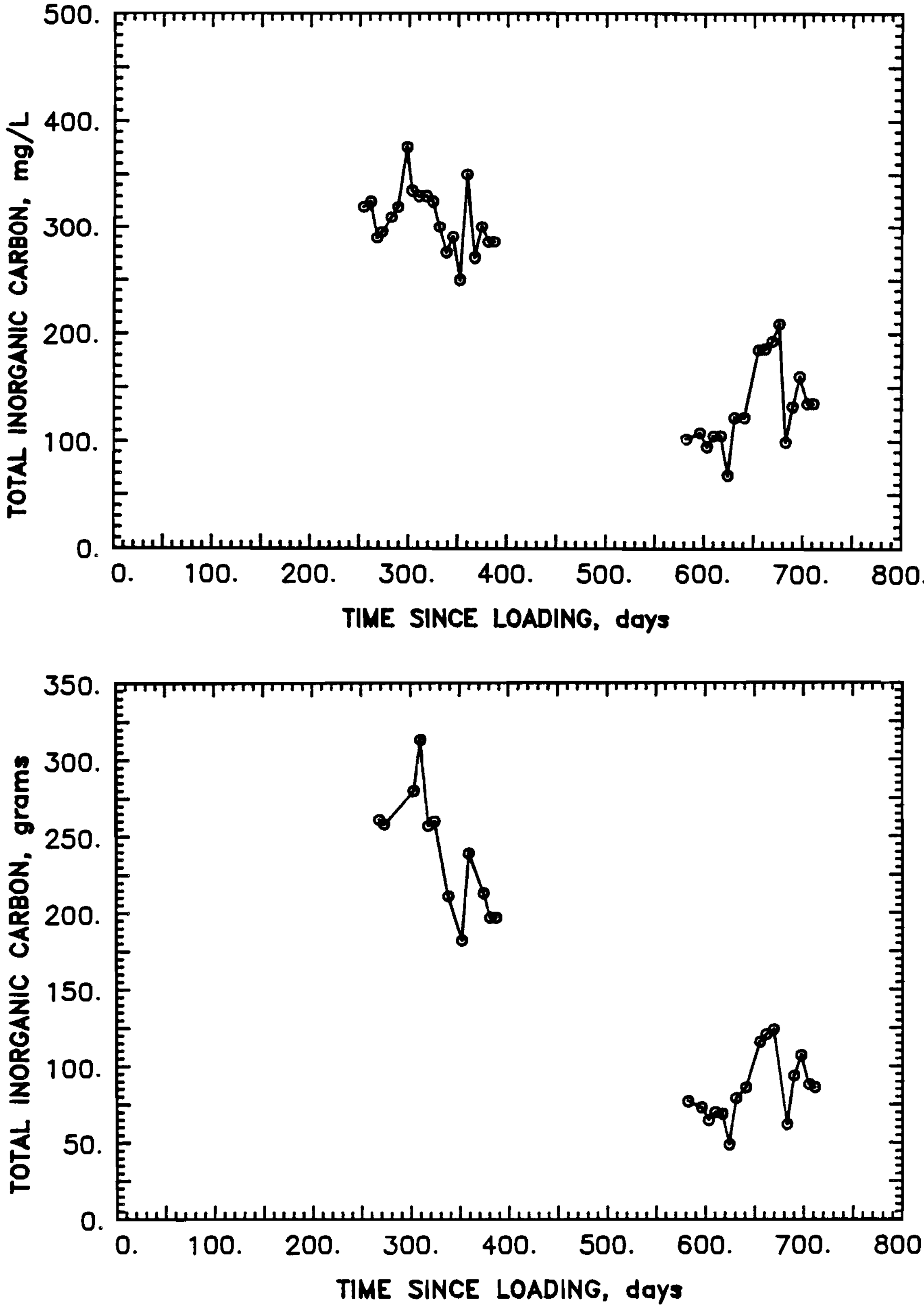
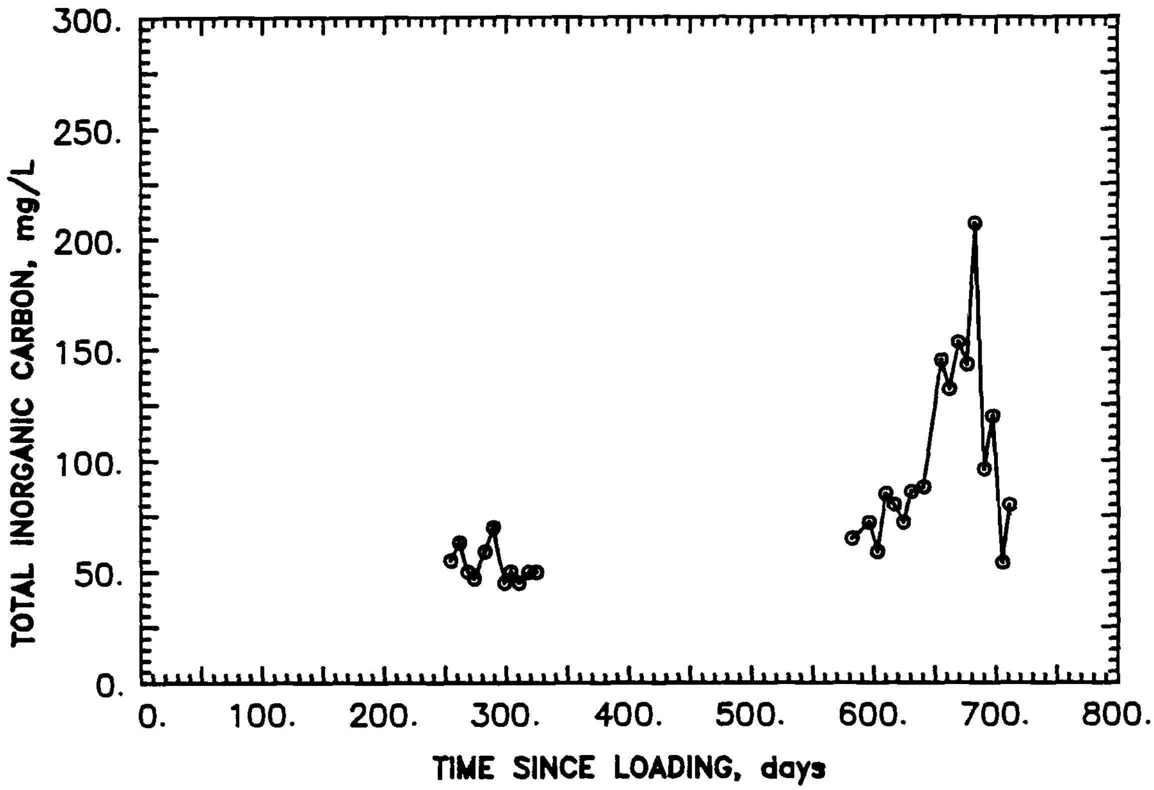


Figure 59. Total Inorganic Carbon Content of Column 1 Leachate



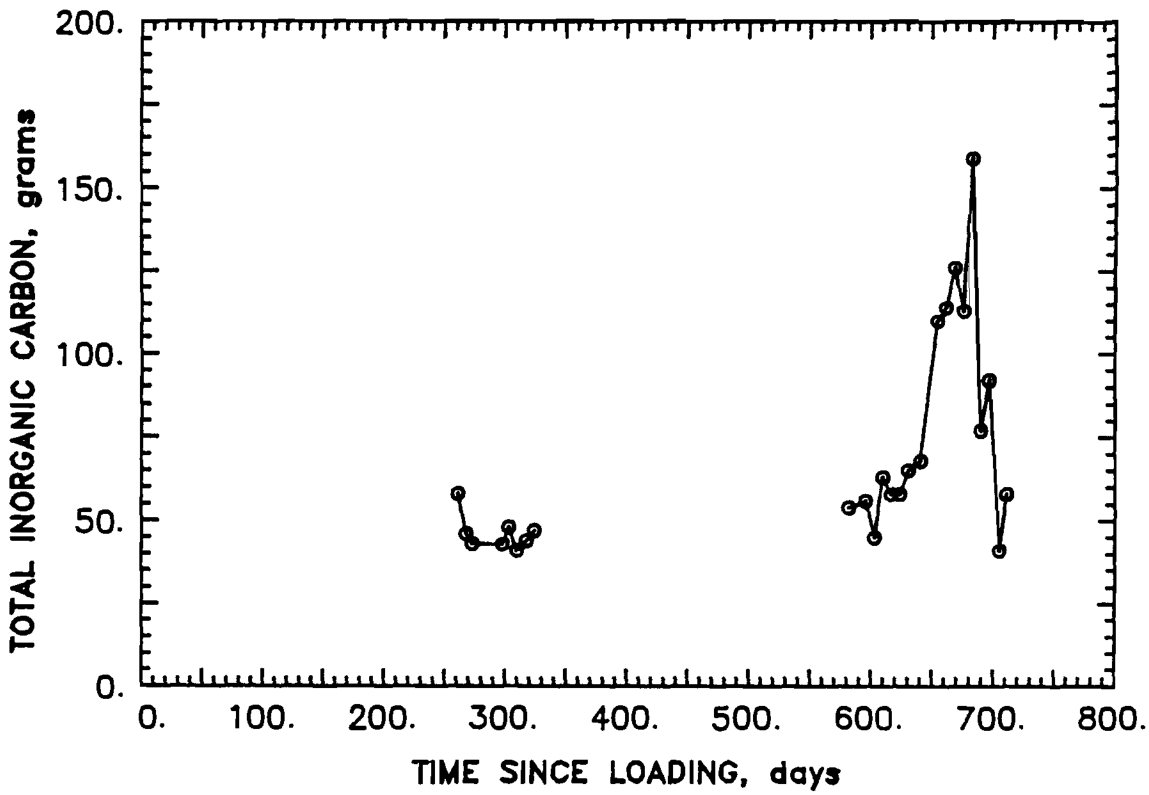


Figure 60. Total Inorganic Carbon Content of Column 2 Leachate

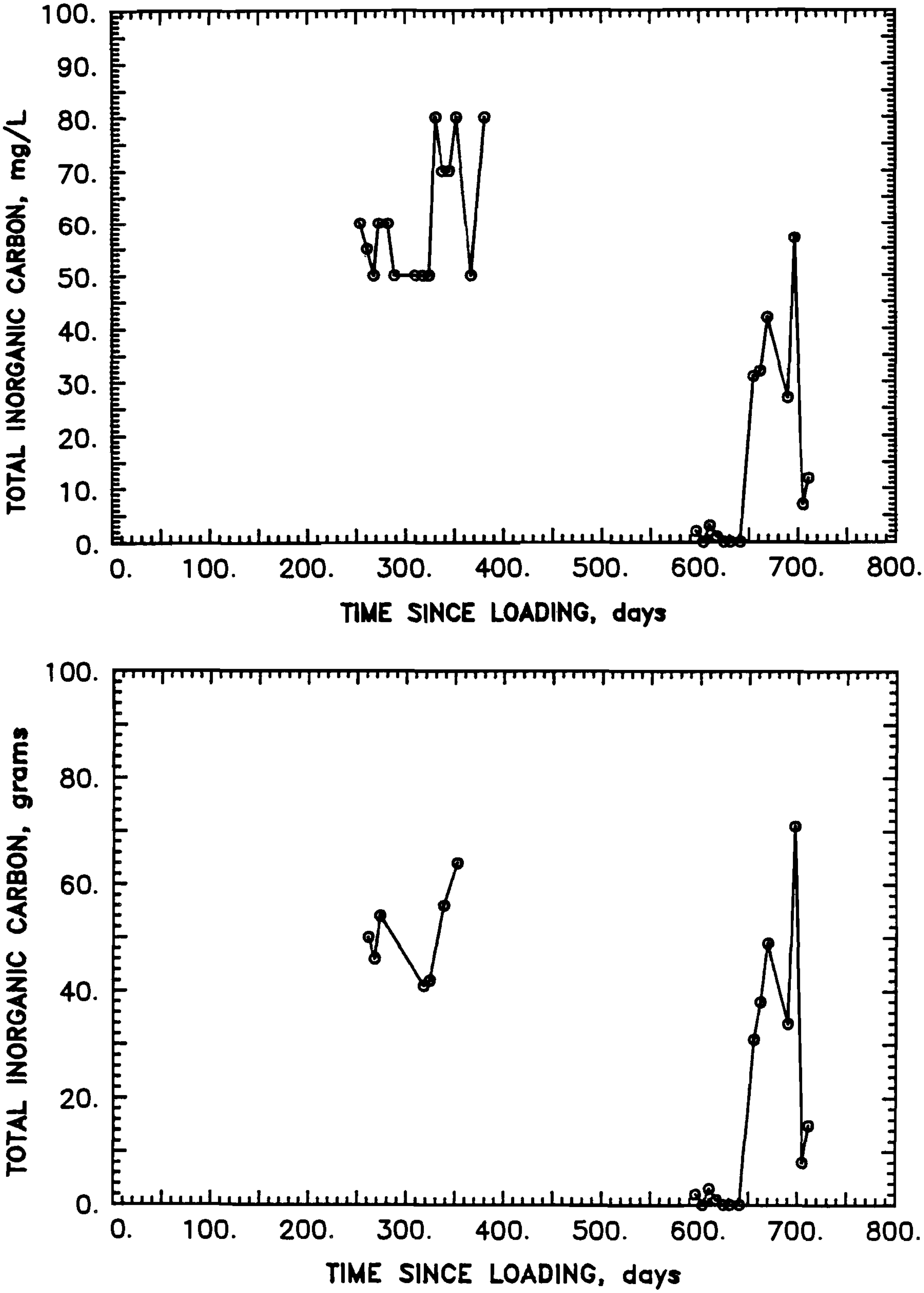


Figure 61. Total Inorganic Carbon Content of Column 3 Leachate

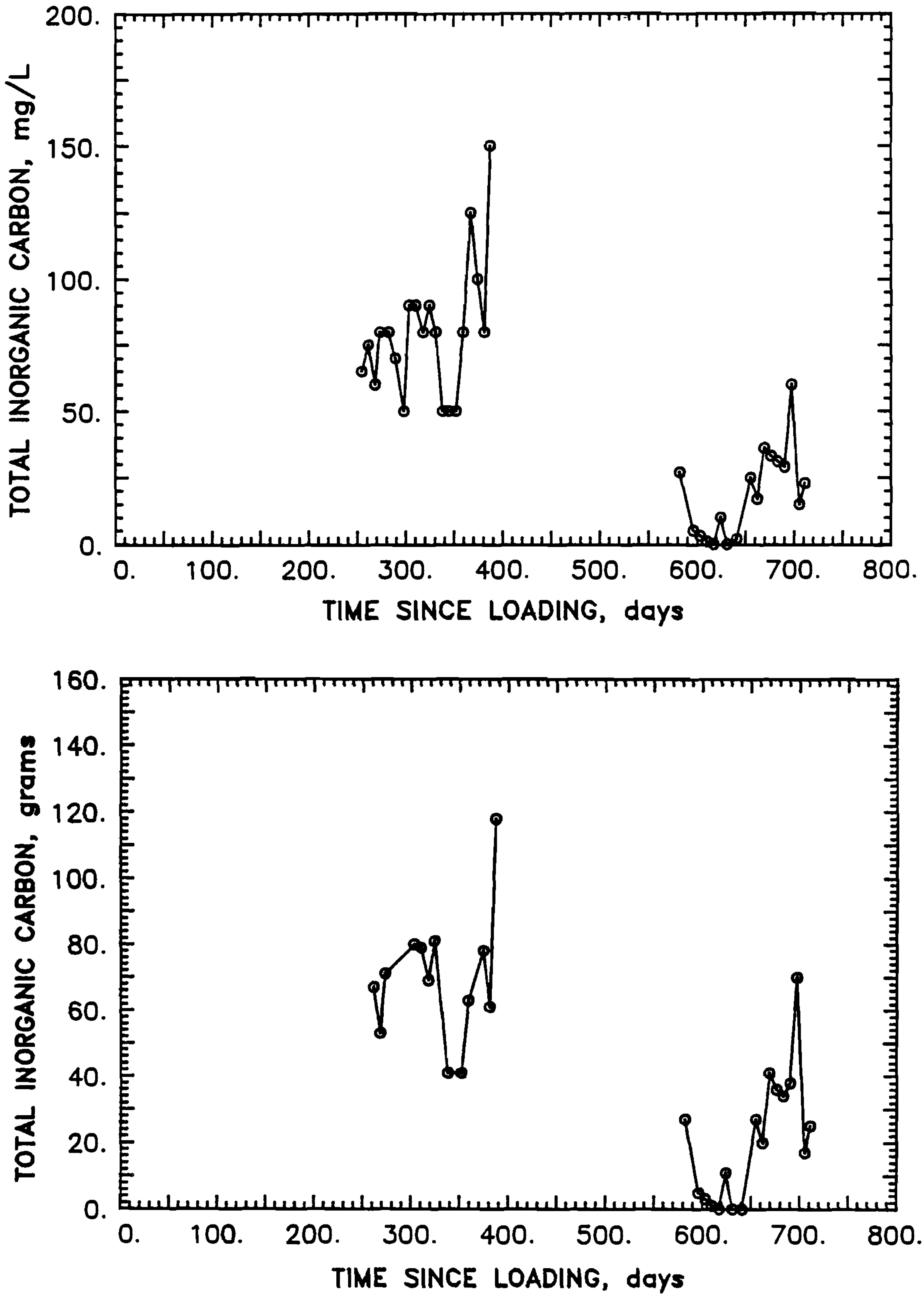


Figure 62. Total Inorganic Carbon Content of Column 4 Leachate

TABLE 21. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR TOTAL VOLATILE ACIDS ANALYSES

Experimental Phase	Days	Operational Characteristics
A	0-150	Initial washout and decomposition
B	150-380	Stabilization or initial accumulation
C	570-640	Post-drought stability or accumulation
D	640-710	Terminal

presence of a clear trend toward lower inorganic carbon levels with increased sludge loadings. The evidence strongly suggests that the carbonate, which is a contributor to the inorganic carbon content of the leachate, was being converted to metal carbonates. Implicit in this process was the conversion of the sludge from the hydroxide form to the generally less soluble carbonate form, a process assuredly facilitated by leachate recycle with its associated opportunity for intimate contact between the recycled leachate and the sludge. Although it was possible that this process was, at least initially, active only at the surfaces of the sludge particles, the overall effect was to encapsulate the toxic metal hydroxides within a less soluble barrier of metal carbonates, thus reducing the potential mobility of the toxic metals. This encapsulation also tended to provide a margin of protection against decreased pH during acid formation by a process analogous to scale provided by the light deposits of calcium carbonate in water distribution systems.

Changes in Nutrients with Time--

The nutrients, phosphorus and nitrogen, are important factors in any consideration of the landfill environment. For example, it is possible that biological activity in landfills might become nutrient limited at times, with concurrent and subsequent impacts on the nature of the landfill environment. In addition, factors which may inhibit biological activity may be reflected in an elevated level of unconsumed nutrients, suggesting the possibility that nutrient trends might be used as an indicator of toxic or inhibitory effects. Finally, the interaction of orthophosphate with a metal sludge containing high levels of calcium, iron and other heavy metals will provide a useful index of the physical condition of the sludge.

The orthophosphate form of phosphorus will not be present as such in domestic refuse in large quantities. Its presence in leachates will arise to a major extent from the hydrolysis of organic phosphates present in materials of biological origin and inorganic polyphosphates such as used in common household detergents. The daily variations in concentrations and masses of orthophosphate observed during the experimental period are presented in Figures 63 through 66. Daily variations in both the concentrations and masses of leachate orthophosphate followed generally similar trends for all four lysimeters, although some differences were evident. Specifically, washout of

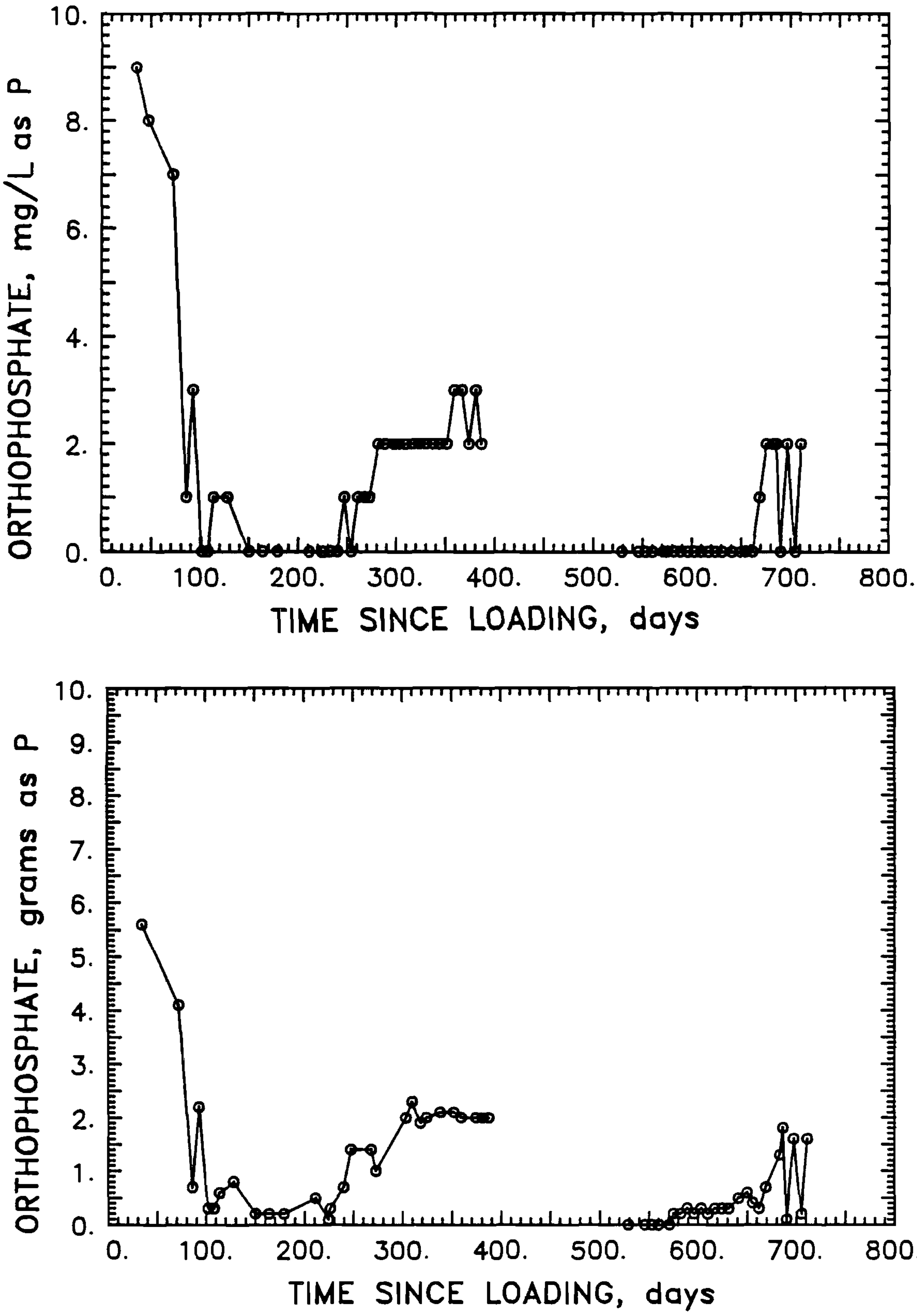


Figure 63. Orthophosphate Content of Column 1 Leachate

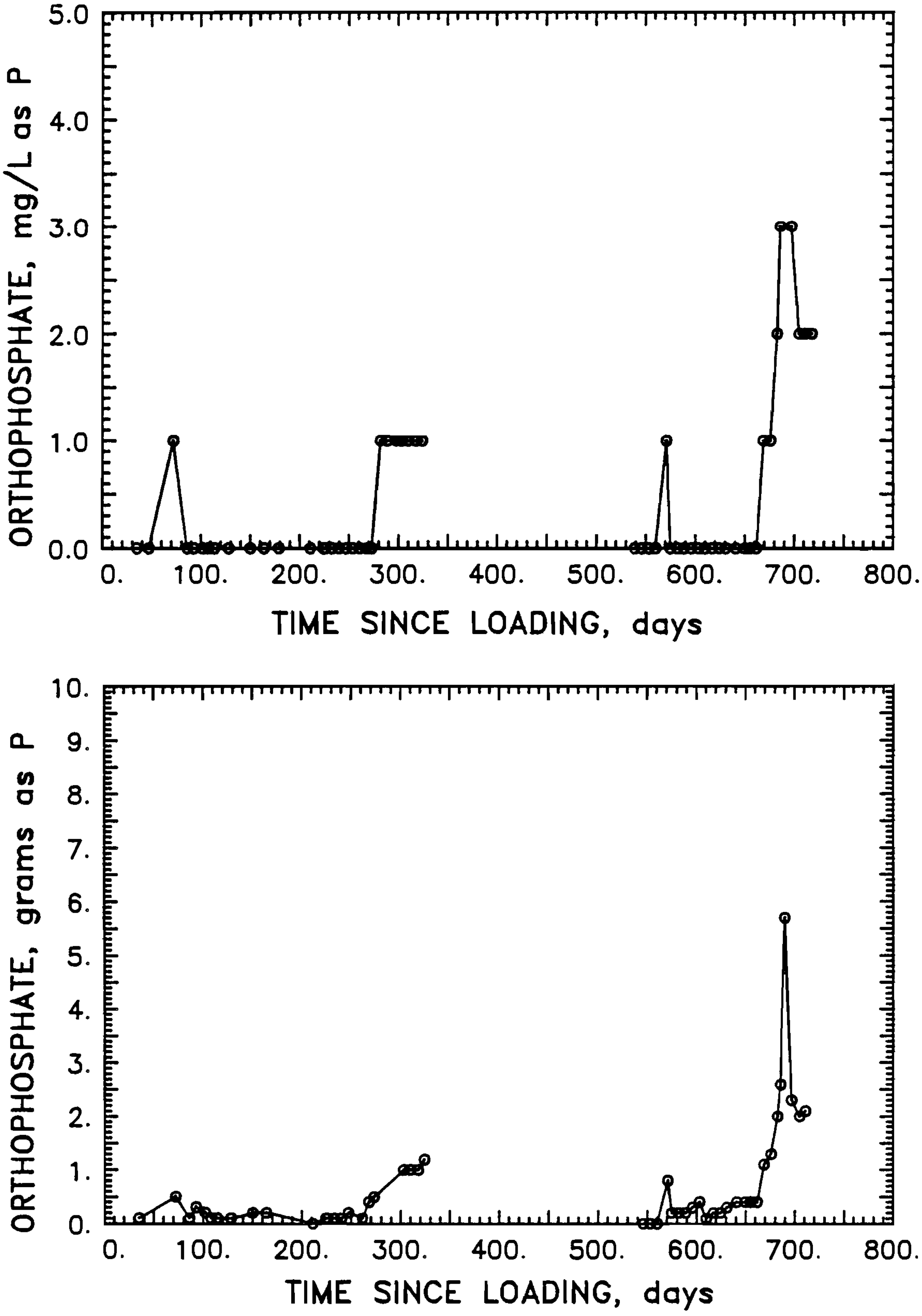


Figure 64. Orthophosphate Content of Column 2 Leachate

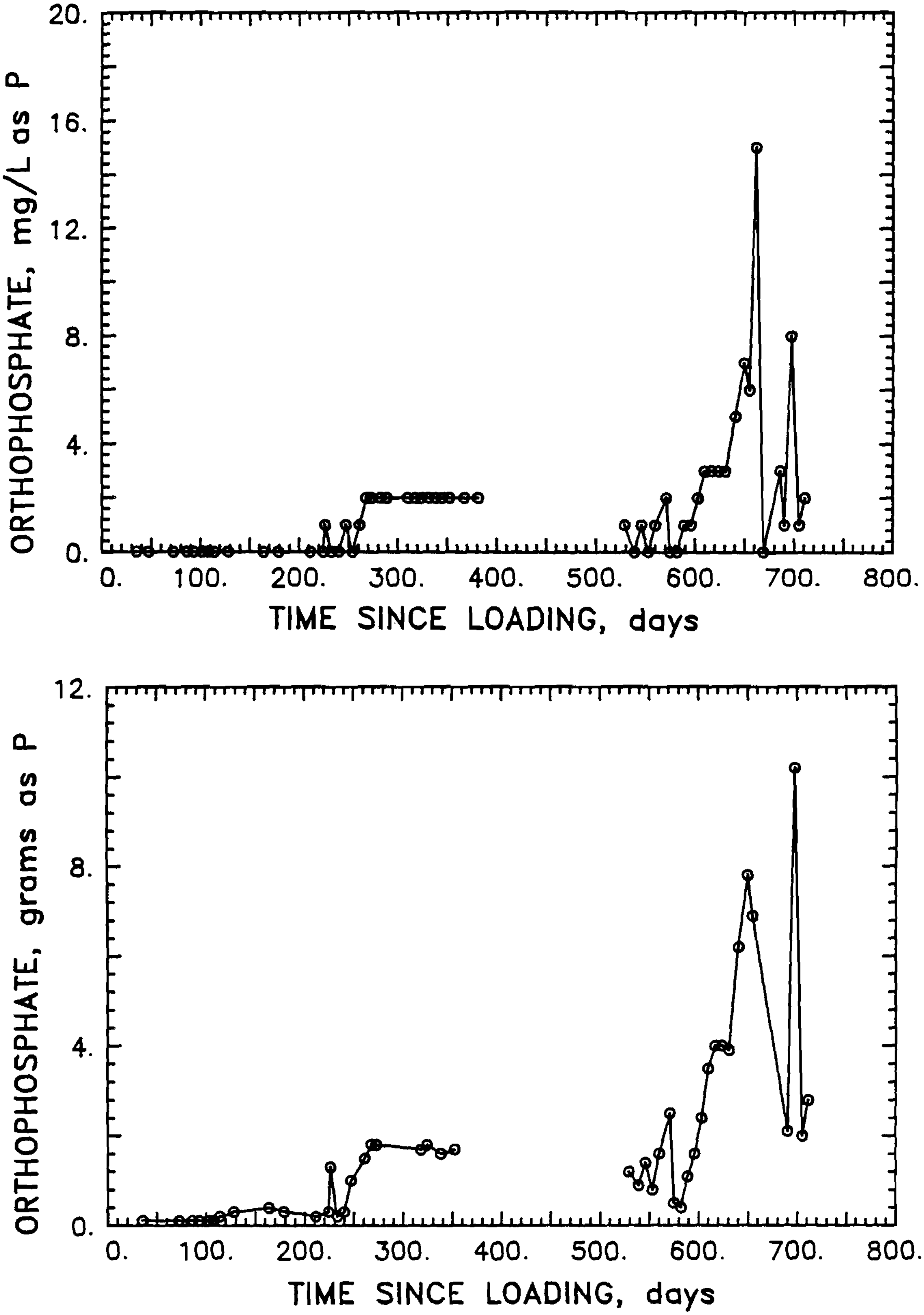


Figure 65. Orthophosphate Content of Column 3 Leachate

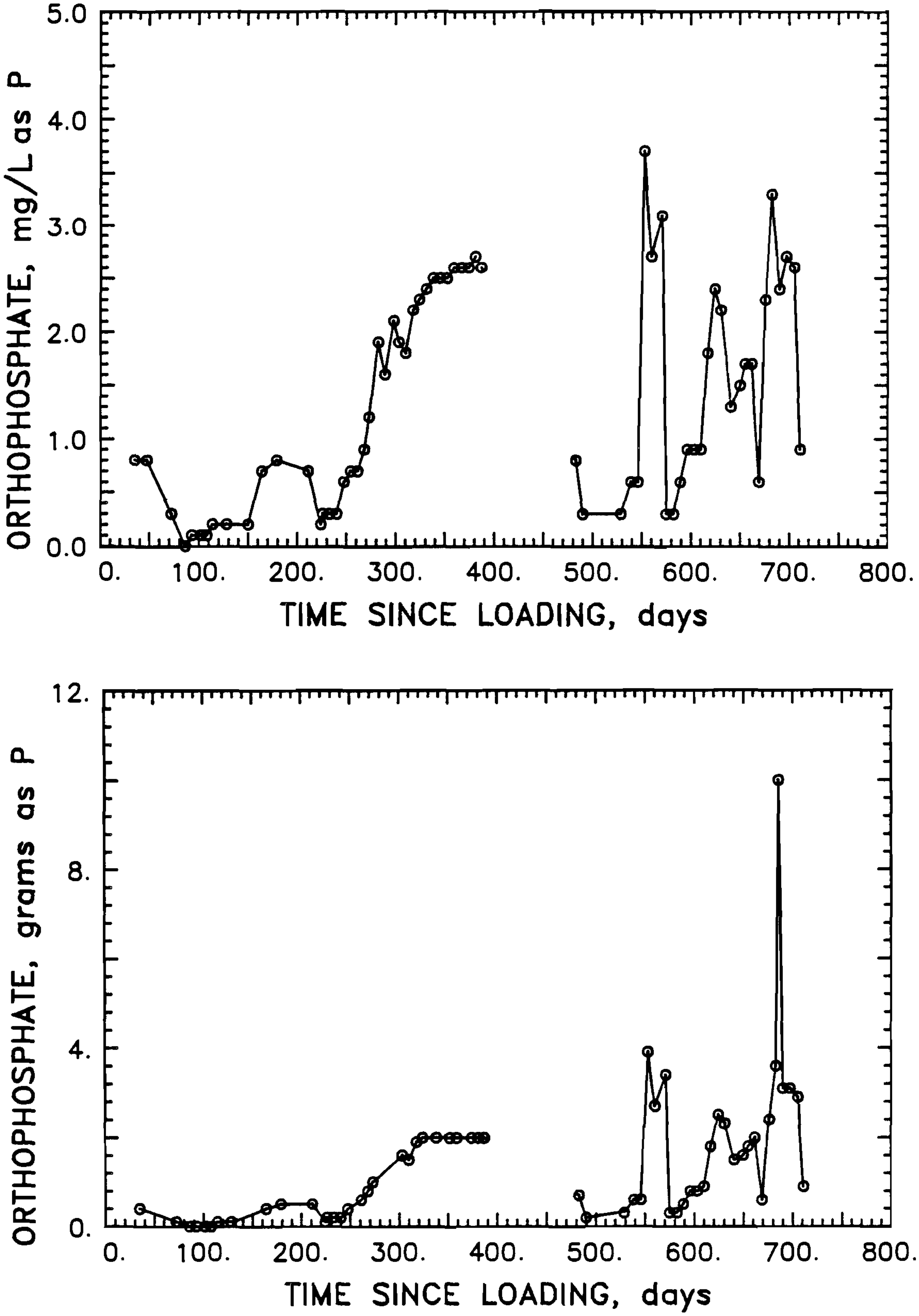


Figure 66. Orthophosphate Content of Column 4 Leachate

phosphate was significant only for Column 1; very low levels were present in the leachate from the metal-laden columns. The difference was likely a consequence of interaction of the phosphate in solution with calcium in the metal sludge and formation of solid hydroxyapatite according to;

$$10\ Ca^{+2} + 6\ PO_4^{-3} + 2OH^- \rightleftarrows Ca_{10}(PO_4)_6(OH)_2 \quad \log K_{so} = 112 \quad \ldots(3)$$

or some interaction of the phosphate with other sludge components such as iron. Following this washout, leachate phosphate concentrations stabilized at low levels for a period of more than 100 days in all columns. This probably reflected uptake of the nutrient by biological activity in combination with continued interaction with metal sludges in Columns 2 through 4, counter-balanced by a gradual release of o-phosphate from solid phosphates and hydrolysis of complex phosphates.

For all columns, the levels of leachate phosphate increased significantly during the period immediately prior to the cessation of leachate generation. This increase in phosphate levels may have been the result of the hydrolysis of complex and organic phosphates combined with a decrease of biological uptake in Column 1 as it approached equilibrium. The increase in phosphate levels in leachates from Columns 2 through 4 may also suggest a diminution in the interaction of this substance with sludge solids. All columns except Column 1 experienced a brief increase in leachate phosphate levels upon resumption of leachate generation, which appeared in the plots of daily data as a sharp spike. No such spike was evident for Column 1 data. It is probable that phosphate generated by hydrolysis of complex and organic phosphates was able to accumulate somewhat in Columns 2 through in which metal inhibition of biological activity seems to have occurred. In Column 1, continued biological activity during the period of drought seems to have been sufficient to consume phosphate, thus preventing the post-drought spike. This interpretation was supported to a degree by the observation that the spike was smallest and of the briefest duration in the leachate from Column 2, the column least influenced by metal inhibition. In addition, Column 2 leachate displayed an extended period (Days 570-670) of low phosphate levels immediately following the intial post-drought spike. In this regard, it was very dissimilar in behavior to Columns 3 and 4 which displayed only a brief decrease in leachate phosphate levels (Days 570-600).

Finally, phosphate levels increased rapidly in the leachate from all four columns immediately prior to termination of sampling. The increase was especially marked for Columns 3 and 4, but occurred in the leachate from Columns 1 and 2 as well. It appeared that phosphate generation had come to exceed biological phosphate consumption by about Day 620-670 in all four columns. In addition, the metal sludges in Columns 2 through had ceased to have any apparent impact in binding phosphate, suggesting that physical encapsulation of the metal sludge by carbonates and sulfides had effectively isolated them from contact with the leachate.

The four discrete experimental phases applicable to leachate orthophosphate for these columns are listed in Table 22. The average values of concentration and mass are presented in Figure 67.

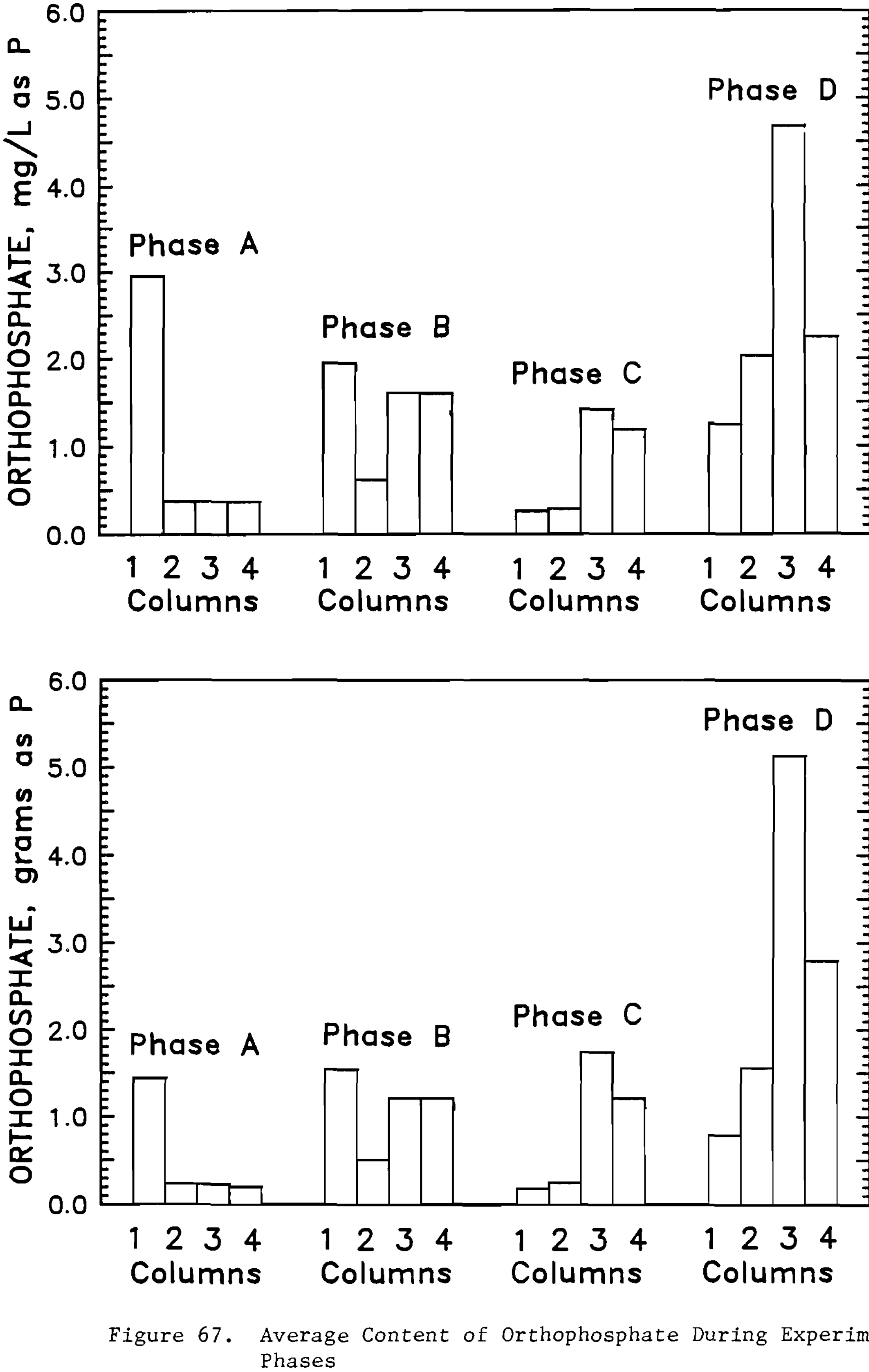


Figure 67. Average Content of Orthophosphate During Experimental Phases

TABLE 22. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR ORTHOPHOSPHATE ANALYSES

Experimental Phase	Day	Operational Characteristicd
A	0-200	Washout
B	200-400	Initial stabilization
C	500-620	Post-drought
D	620-730	Terminal

Examination of the production phase data indicates that while the sludge had a substantial impact on orthophosphate behavior in these columns, the impact was complex and difficult to interpret. In the sludge-free control column, the initial moderate levels of leachate orthophosphate were substantially unchanged during the first two phases of column operation. This indicates that the initial rapid consumption of orthophosphate was later compensated for in the pre-drought period by decomposition of organic and polyphosphates. The considerable decrease in leachate orthophosphate levels during Phase C may have resulted from biological consumption in excess of generation, while a distinct increase in orthophosphate levels suggestive of increased hydrolytic activity was noted in the terminal phase of column operation.

The sludge-laden columns displayed significantly different behavior. During the washout phase, the binding by the metal sludge was obvious with all three columns having extremely low leachate orthophosphate levels. Beyond the washout phase, the behavior of the orthophosphate is more difficult to rationalize. Although immobilization of the orthophosphate by the metal sludge would be expected to be an important process here, the orthophosphate levels actually tended to increase with increasing sludge loadings. There exist four possible mechanisms which may have been operational, two of which, the previously mentioned chemical immobilization of orthophosphate and biological uptake, acted to reduce orthophosphate concentrations and two of which, hydrolysis of organic and polyphosphates and release of orthophosphate bound to the sludge as a result of the interaction of these solid phosphates with such species as sulfide, tended to increase the concentration of orthophosphate. There was an obvious trend toward increasing concentrations of orthophosphate in all sludge-laden columns during the terminal phase of column operation, indicating a dominance of generative over consumptive processes. Beyond this, the data available are insufficient to provide a more detailed rationalization for this behavior.

In comparison with phosphorus, the sources of soluble reduced nitrogen in the columns included compounds of biological origin contained in food wastes and other organic debris. These compounds will participate in a complex array of biological and chemical reactions including hydrolysis reactions, decomposition of proteins and deamination of amino acids yielding ammonia, nitrification processes by which the ammonia will be converted into nitrate and nitrite, and reductive processes which will convert the nitrate back to ammonia. In addition, the ammonia and nitrogenous organic compounds such as amino acids may undergo reactions producing more complex compounds such as peptides and proteins which were detected by the column leachate analyses. It is obvious that, of the parameters monitored in these studies, TKN was the most complex in terms of both sources and behavior. This complexity is reflected in the temporal behavior of the TKN in the leachates from these columns.

Levels of leachate TKN as a function of time are presented in Figures 68 through 71. While the data are characterized by substantial scatter, the pre-drought trends were remarkably uniform. There was an initial rapid washout of TKN with levels reaching minimum values at approximately Day 200. A steady increase followed up to the time at which leachate production ceased. Significantly, although initial leachate TKN levels were similar for all four columns, the level for Column 1 decreased by about 90 percent to the 200-day minimum, while the decreases for Columns 2, 3 and 4 were only about 45 percent the curves for Columns 2, 3 and 4 being virtually identical. Between the minimum point and the cessation of leachate production, leachate TKN values recovered to levels approximating the intial values for all four columns. These results suggested a selective inhibition of TKN consumption at all sludge loadings, while the TKN generation processes manifested between Day 200 and cessation of leachate generation were reaatove;u uninhibited.

The column behavior following the drought was somewhat more complex. Columns 1 and 2 both displayed leachate TKN levels similar to the prior Column 1 minimum at Day 200. Apparently the prolonged quiescent period was sufficient to allow TKN consumptive processes in the low sludge column (Column 2) to proceed to near completion. The levels of TKN in the more heavily sludge-laden columns (Columns 3 and 4) were substantially higher at the resumption of leachate generation, indicating that the level of inhibition in these columns exceeded the ability of the TKN consumption processes to adapt. Beyond this point, the levels of leachate TKN for Column 1 increased to a level approximating that attained immediately prior to the drought, while the levels for Columns 2, 3 and 4 showed little change. It is possible that the inhibition of biological activity combined with physicochemical interactions between dissolved TKN and metal sludge solids had the effect of stabilizing the TKN levels in Columns 2, 3 and 4.

The experimental phases applicable to leachate TKN levels observed in this research are summarized in Table 23. The average levels of leachate TKN during the operational phases are presented in Figure 72. These averages conformed clearly to the trends detailed above. Average levels for Column 1 tended to be less variable than in the other three columns, reflecting a balanced and uninhibited biological processes. Columns 3 and 4 showed strong inhibition while the behavior of Column 2 was transitional and suggested partial inhibition.

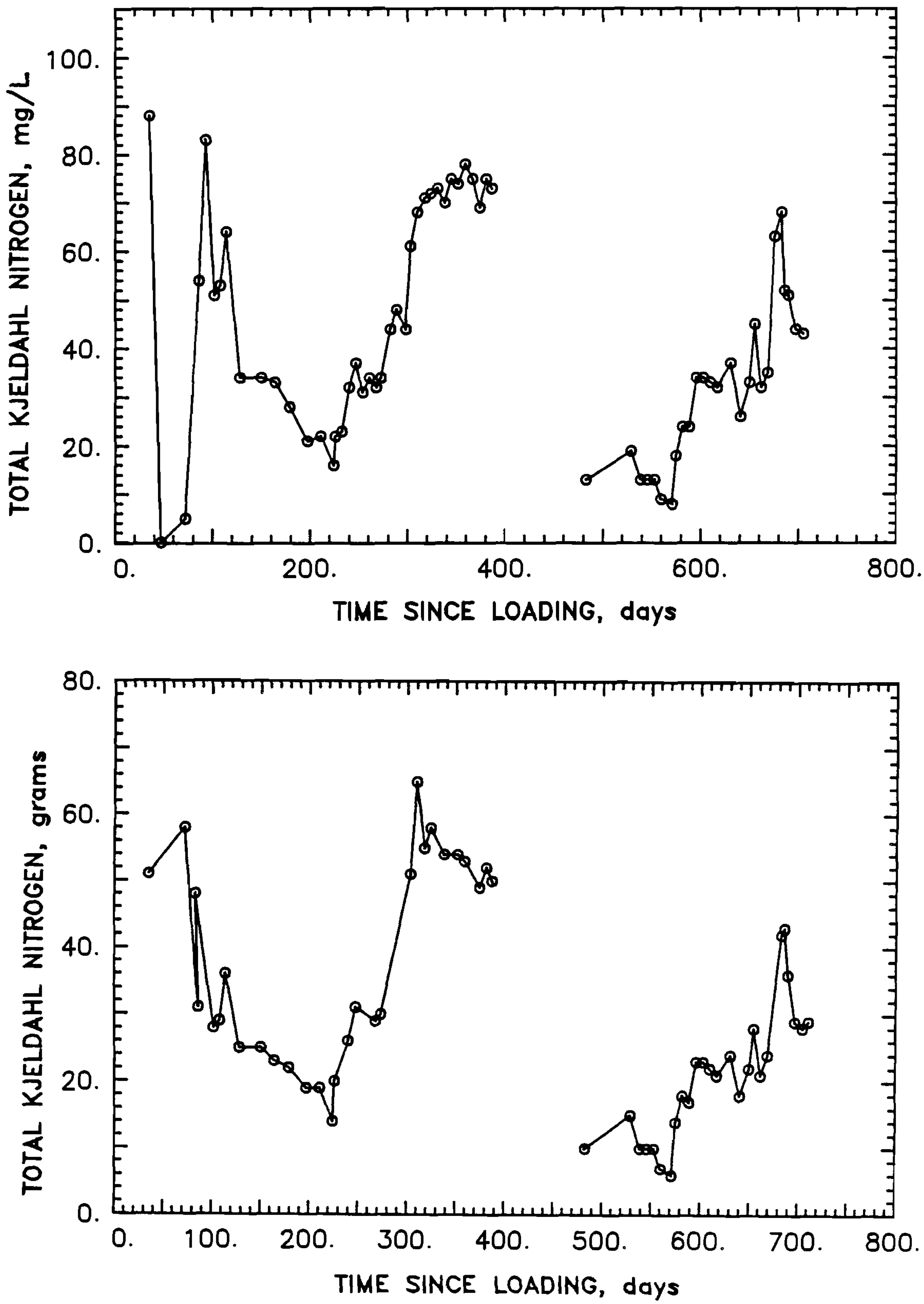
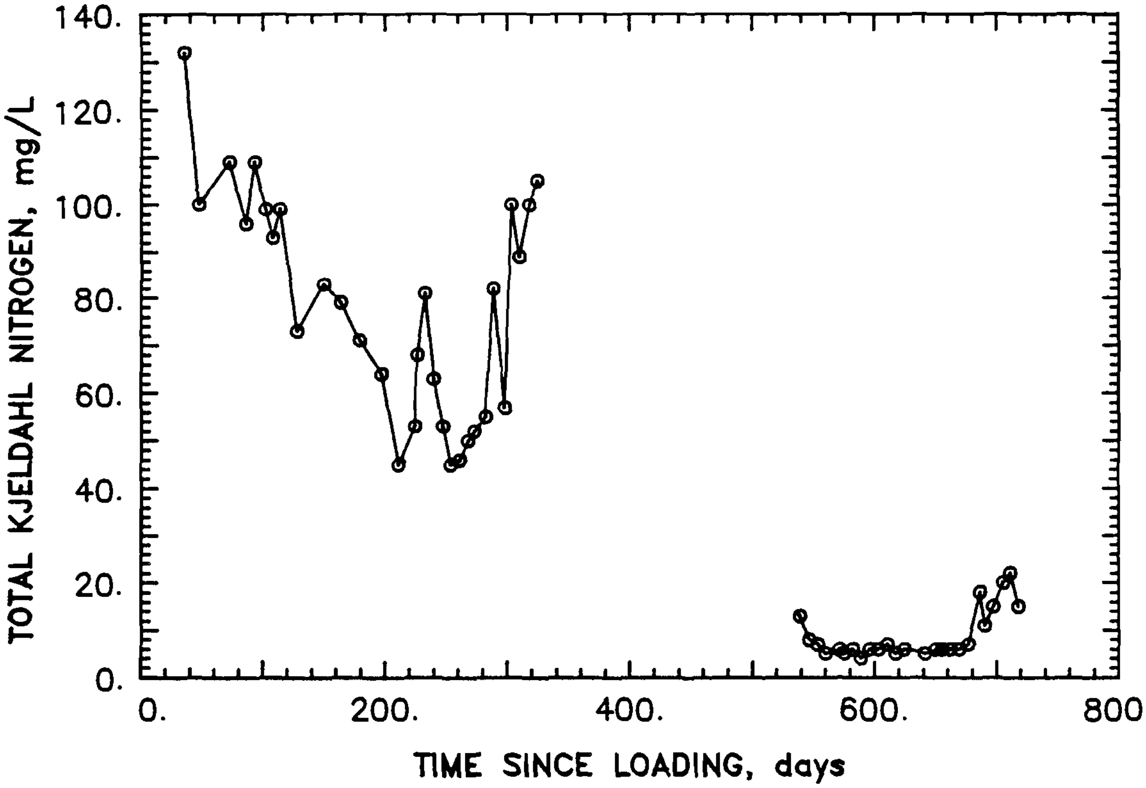


Figure 68. Total Kjeldahl Nitrogen Content of Column 1 Leachate



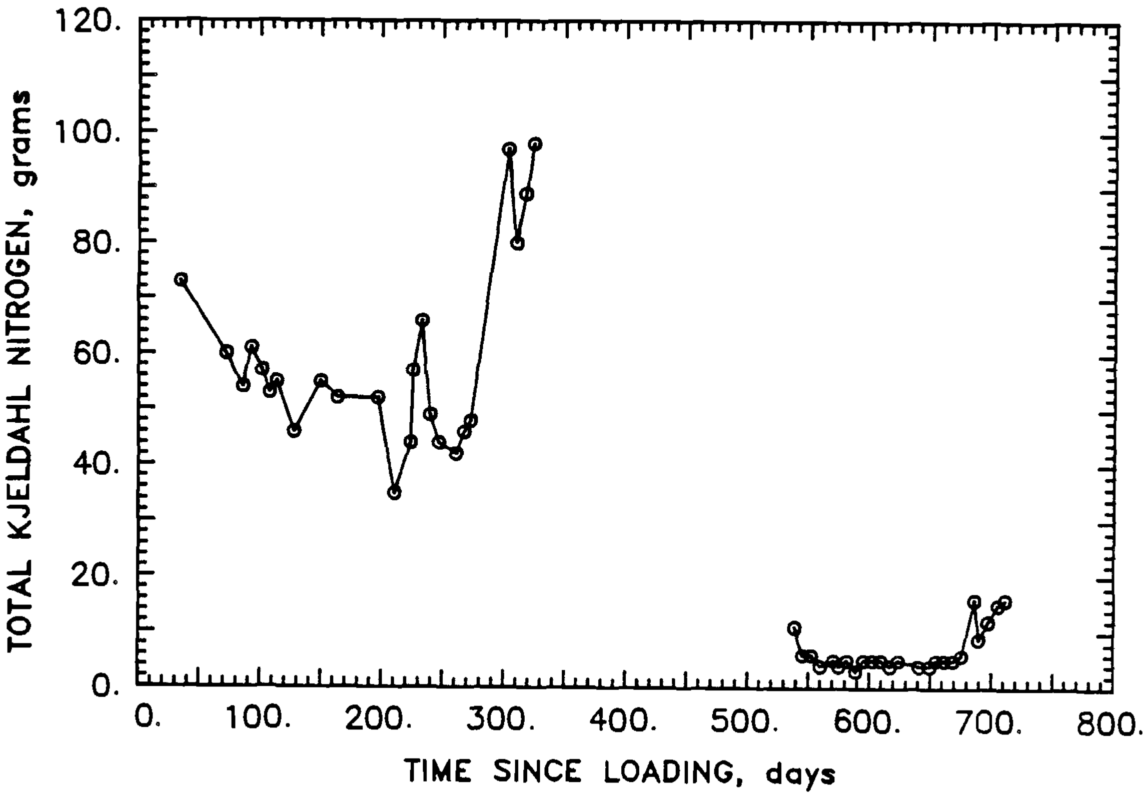


Figure 69. Total Kjeldahl Nitrogen Content of Column 1 Leachate

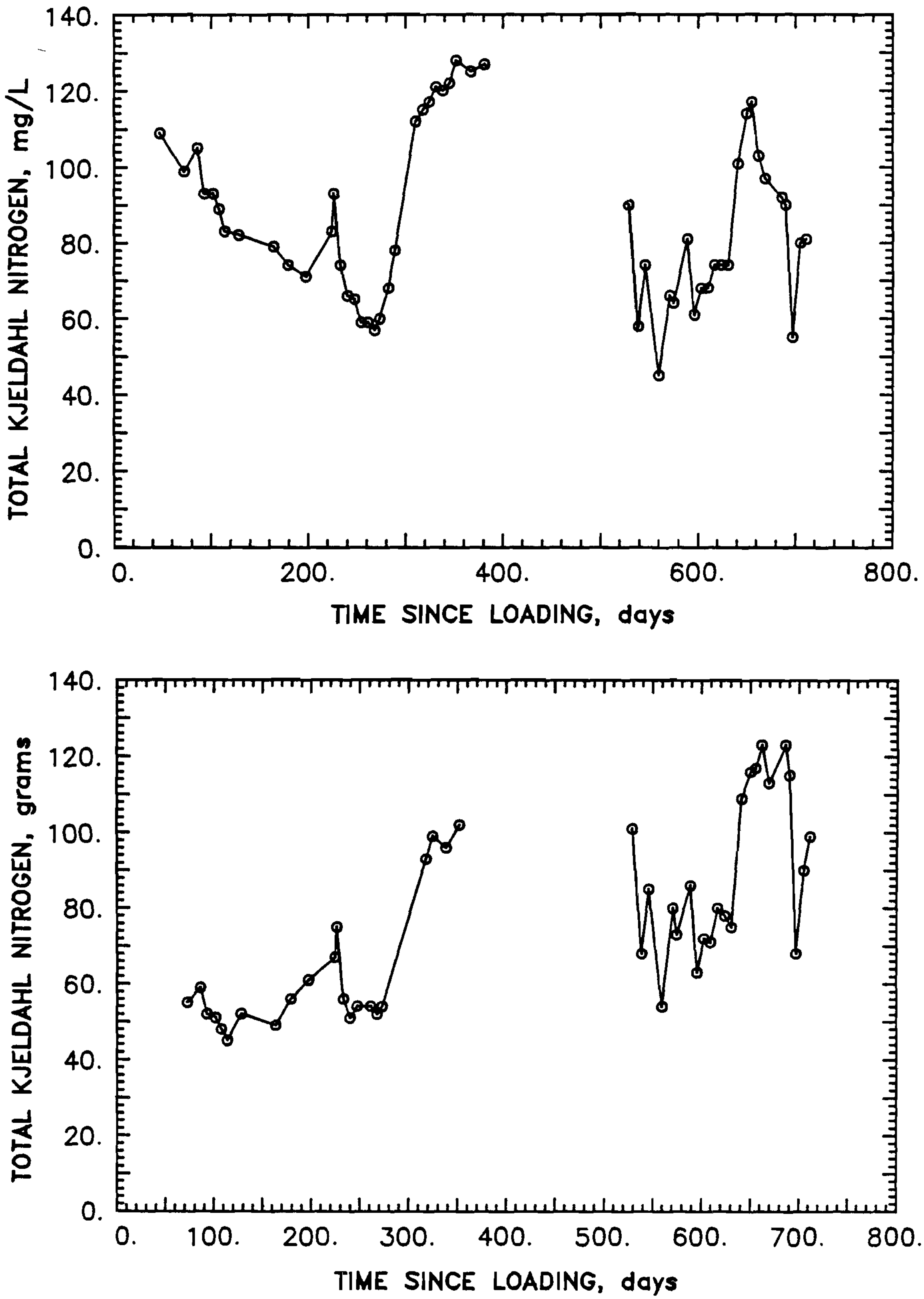
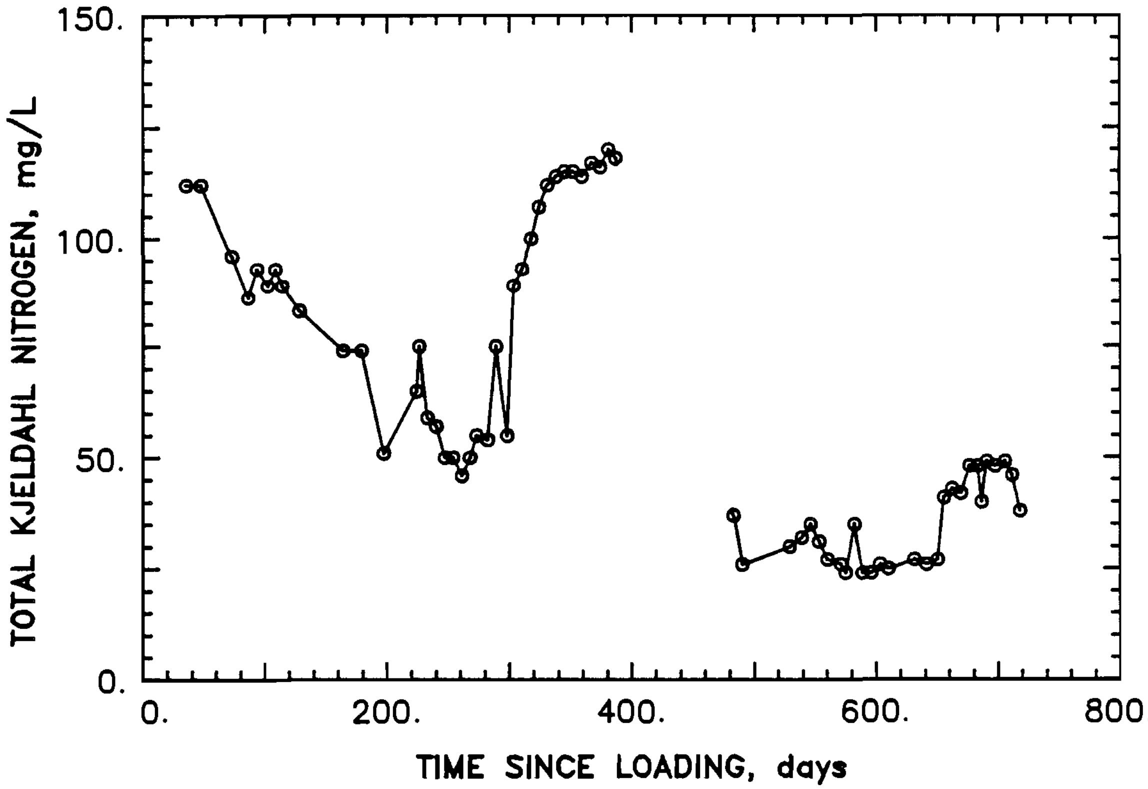


Figure 70. Total Kjeldahl Nitrogen Content of Column 3 Leachate



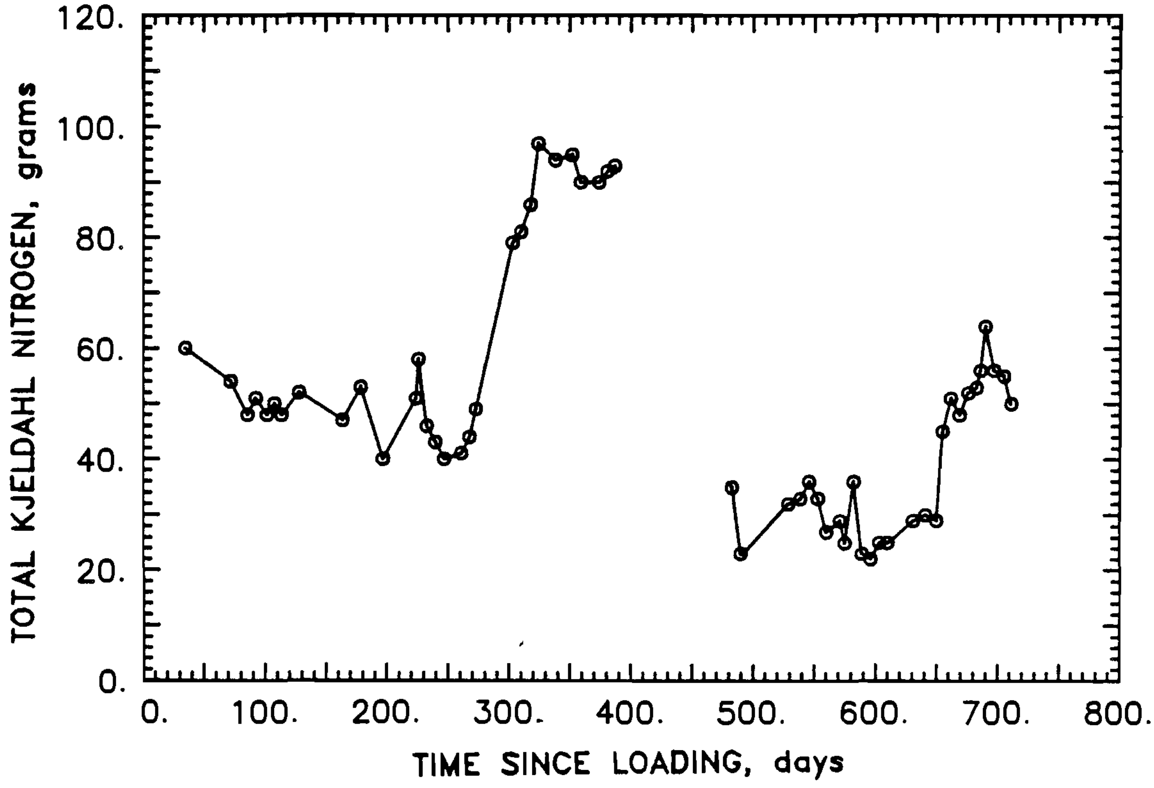
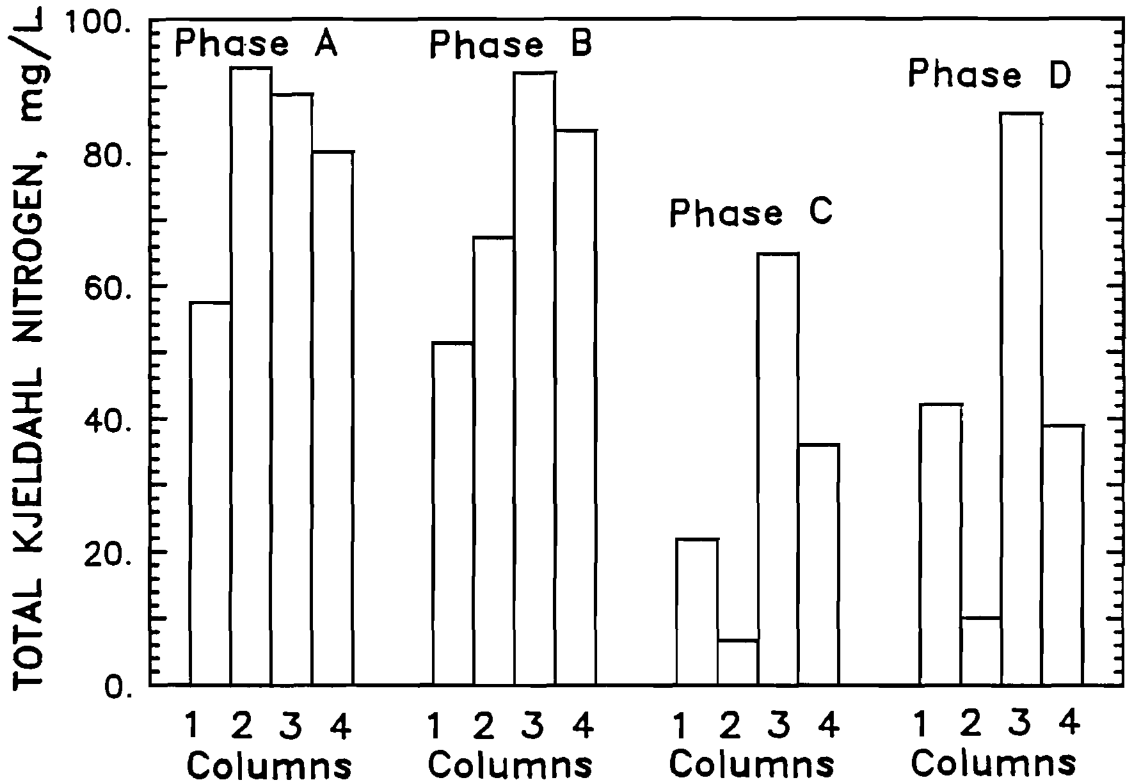


Figure 71. Total Kjeldahl Nitrogen Content of Column 4 Leachate



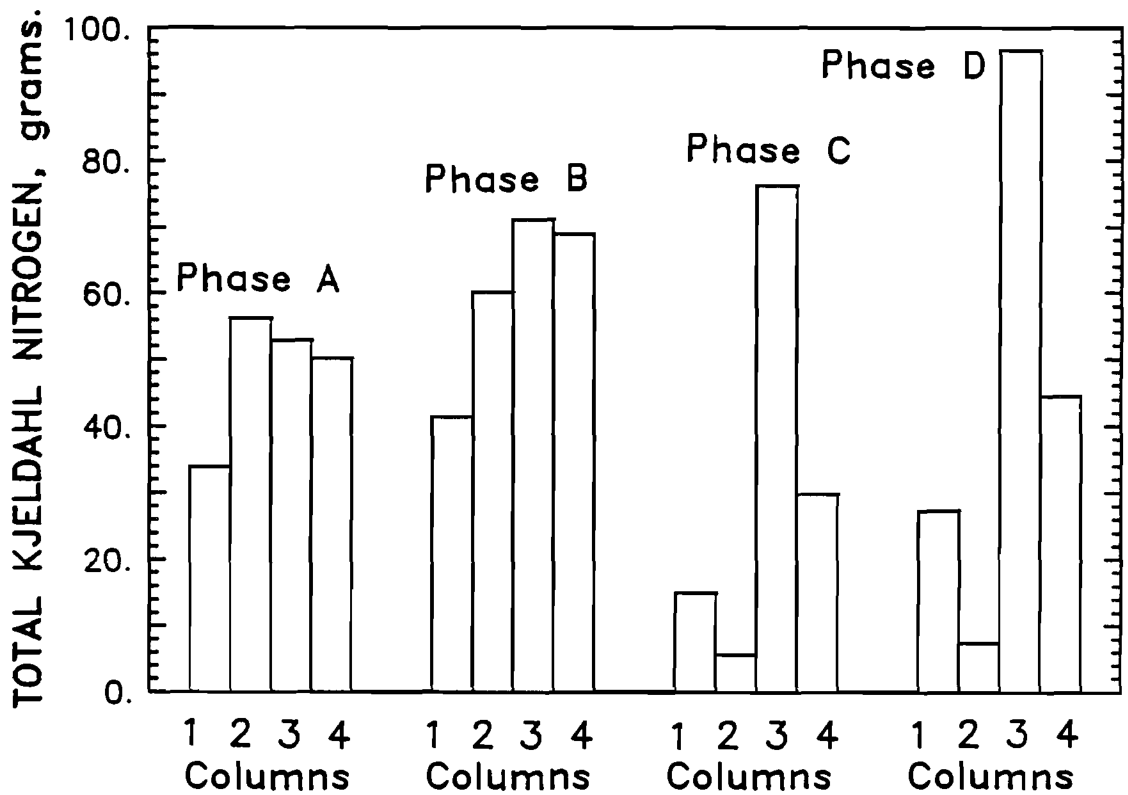


Figure 72. Average Content of Total Kjeldahl Nitrogen During Experimental Phases

TABLE 23. PHASES OF SIMULATED LANDFILL OPERATIONS APPLICABLE FOR TOTAL KJELDAHL NITROGEN ANALYSES

Experimental Phase	Days	Operational Characteristics
A	0-200	Washout
B	200-400	TKN recovery
C	480-600	Post-drought
D	650-730	Terminal

Environmental Factors Controlling Metal Solubility

The following characteristics of landfill leachate were determined to impact heavy metal solubility.

pH--

The pH is a major determinant of the behavior of all leachate contaminants, including metals. In general, metal solubility will tend to increase as pH decreases. Therefore, the progress of landfill stabilization through acid formation and consumption will signficantly influence pH and associated heavy metal solubility behavior.

Redox Potential--

The chemical environment of a sanitary landfill is typically reducing due to biologically mediated oxidation-reduction reactions and limited access to atmospheric oxygen. This condition will impact heavy metal mobility in two ways. First, where a choice exists between the oxidized and reduced form of a metal, e.g., Fe^{+3}/Fe^{+2}, the reducing potentials will favor the reduced species over the oxidized. Secondly, the reducing conditions will facilitate reduction of sulfate to sulfide. Since sulfide is a powerful precipitant for many heavy metals, the formation of this species will provide a mechanism by which toxic heavy metals can be immobilized even at relatively low pH conditions.

Complexing Agents--

While leachates will contain an abundance of potential metal precipitants (S^{-2}, CO_3^{-2}, OH^-), they will also be rich in potential complexing ligands. These latter materials are mostly organic in nature and will compete with the precipitants for reaction opportunity with the metals and, thereby, increase metal solubility in accordance with Equation 4.

$$MA(s) + L \rightleftarrows ML\ (aq) + A \qquad \ldots(4)$$

where; MA = any solid metal salt
L = ligand
ML = metal ligand complex (e.g., $FeS(s) + EDTA = Fe(EDTA) + S^{-2}$)
A = anion

pH and Precipitating Anions--

Leachate pH (Figures 73 through 76) will have the impact of determining the distribution of those anions most commonly available in leachates as precipitants, i.e., sulfide, carbonate and hydroxide. Figure 77 illustrates a typical pH-pC diagram for these three species. Since the solubility of a given metal is defined by Equation 5,

$$[M] = K_{so}/[A]^n \qquad ...(5)$$

where: $[M]$ = solubility of the metal;
$[A]$ = concentration of the anion;
n = number of anions in MA_n; and,
K_{so} = the solubility product,

it is clear that metal solubility will be strongly pH dependent. In a typical landfill, the controlling species for most heavy metals will be sulfide. Figure 78 is a pH-pC diagram for the predicted saturation concentrations of several metals in equilibrium with a 0.02 $\underline{M}$ total concentration (C_t) of sulfides, where C_t is defined as:

$$C_t = [H_2S] + [HS^-] + [S^{-2}] \qquad ...(6)$$

From this illustration, it is obvious that the saturation solubilities of these metals are very low in spite of being in equilibrium with correspondingly low concentrations of S^{-2} (Figure 78). However, trivalent chromium is an exception among the more common heavy metals in that its solubility is not controlled by sulfide equilibria but by hydroxide equilibria. This behavior could present potential problems, since the equilibriumconcentration of Cr^{+3} would be as high as 200 mg/L at a pH of 5, a typically low pH for a leachate during the acid phase of landfill stabilization. Thus, although the solubility of chromium decreases fairly rapidly with increasing pH, it will be among the more mobile of the heavy metals in a typical landfill leachate. In contrast, with an abundance of alkaline materials, such as the hydroxide sludge employed in these investigations, mobility of chromium would be greatly reduced.

In those rare cases where sulfide concentrations are very low or have been depleted due to their removal or the possible reinstatement of oxidizing conditions, the fate of the heavy metals becomes considerably more complex. With sulfide concentrations as low as 10^{-6} molar, the removal of zinc would no longer be controlled by sulfide and would, like chromium, depend upon the hydroxide equilibria. However, superimposed on this reaction would also be the relative influence of the carbonate-bicarbonate equilibrium which would, in the absence of sulfide, help determine the probable precipitating species. For instance, assuming an alkalinity as $CaCO_3$ of 2000 mg/L and a pH of 6.5 in the absence of sulfides, the probable precipitating species would be $CdCO_3$, $Cu_3(CO_3)_2(OH)_2$, $PbCO_3$ and $Cr(OH)_3$. Zinc and nickel would be least likely to precipitate, probably as respective carbonate and hydroxy-carbonate species,

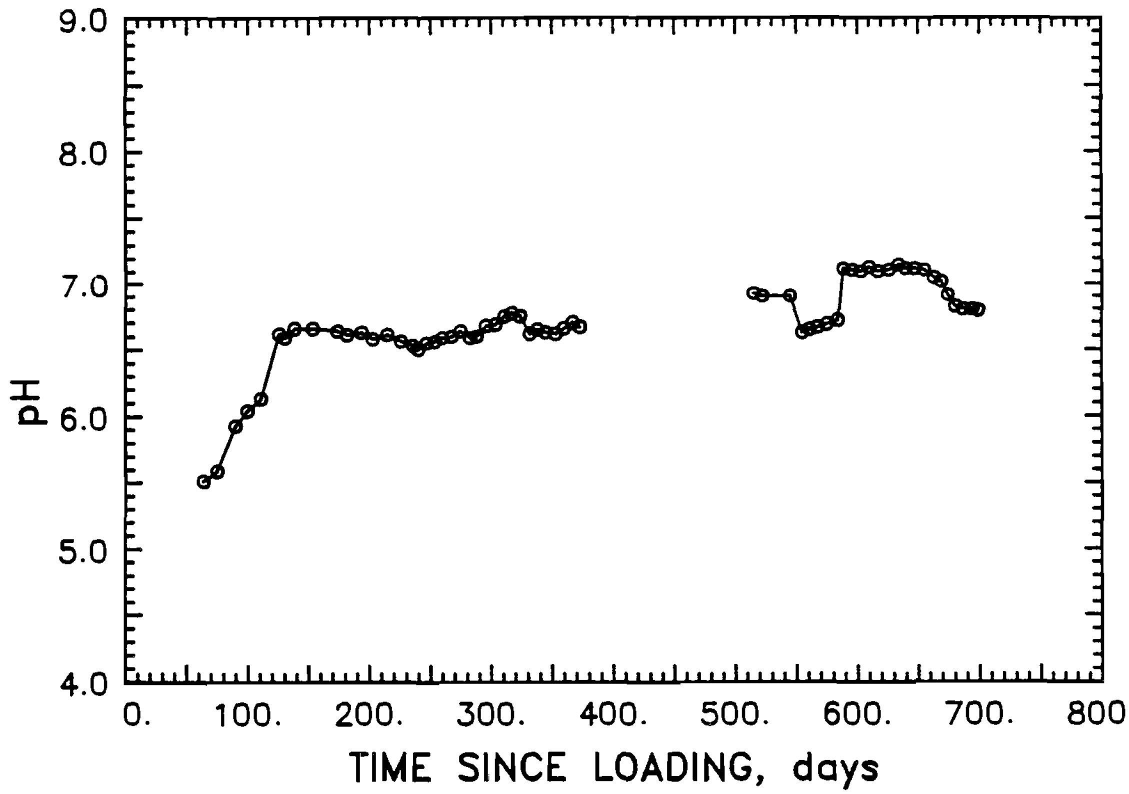


Figure 73. pH of Column 1 Leachate

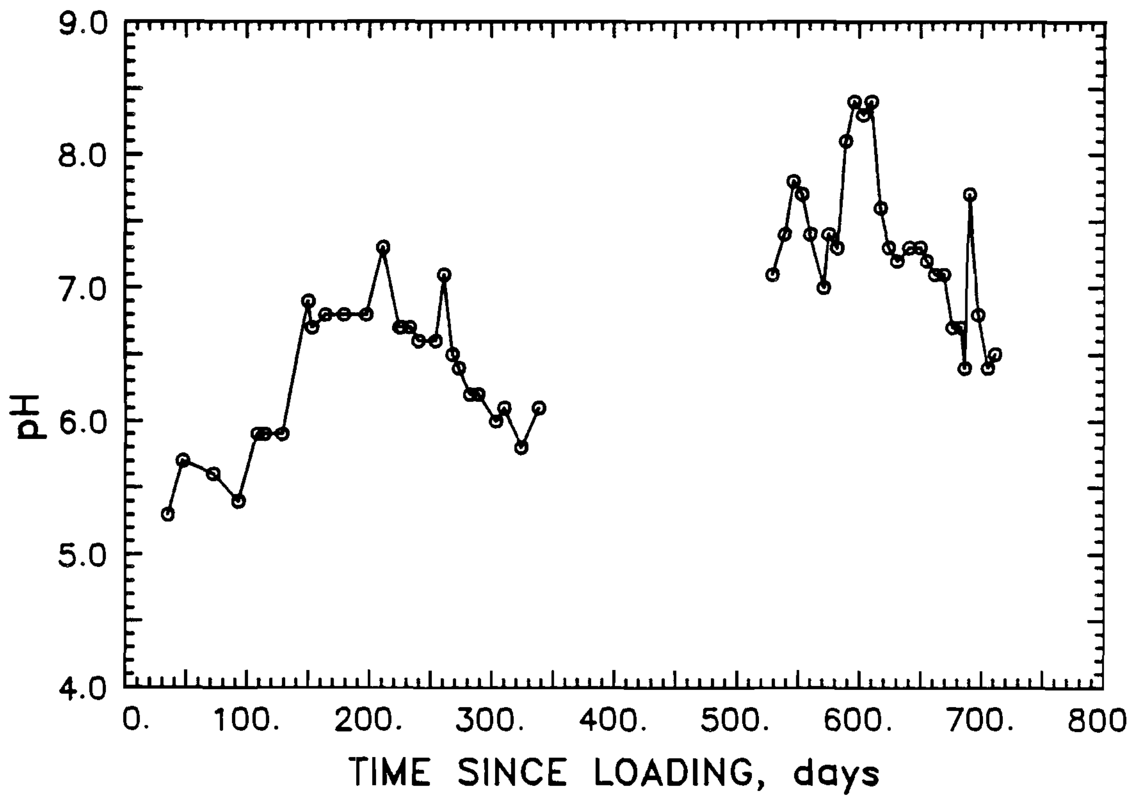


Figure 74. pH of Column 2 Leachate

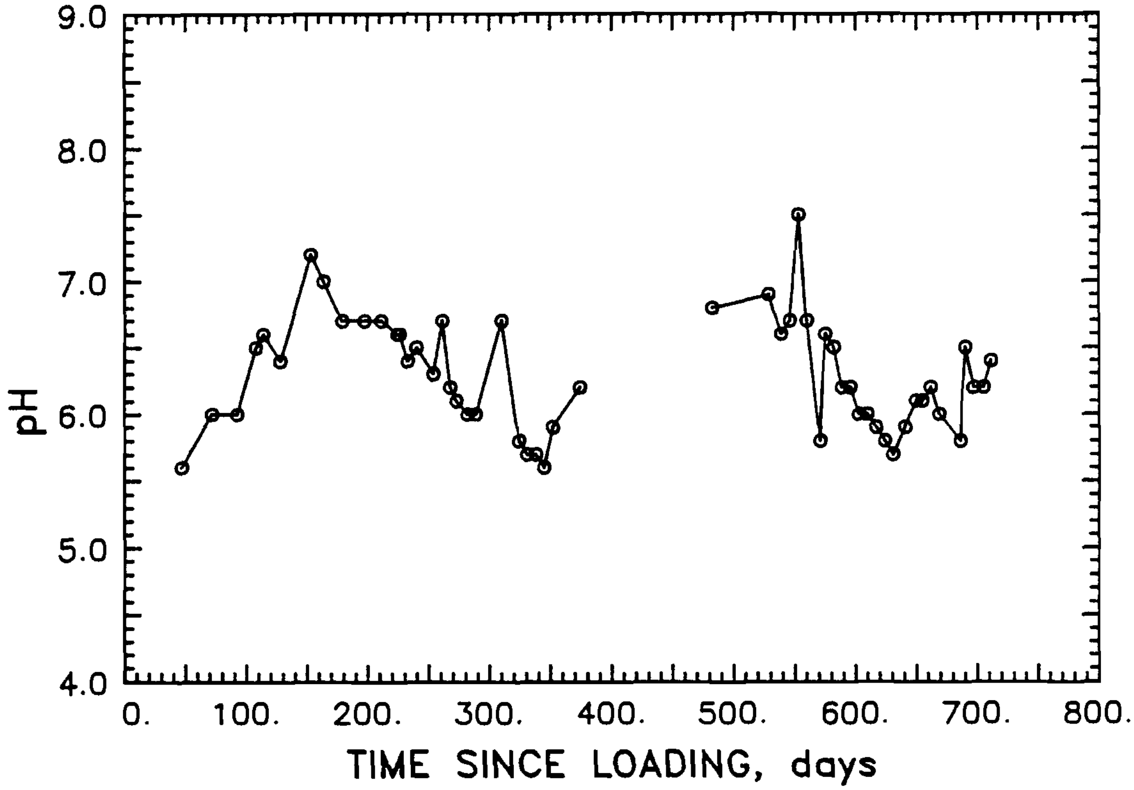


Figure 75. pH of Column 3 Leachate

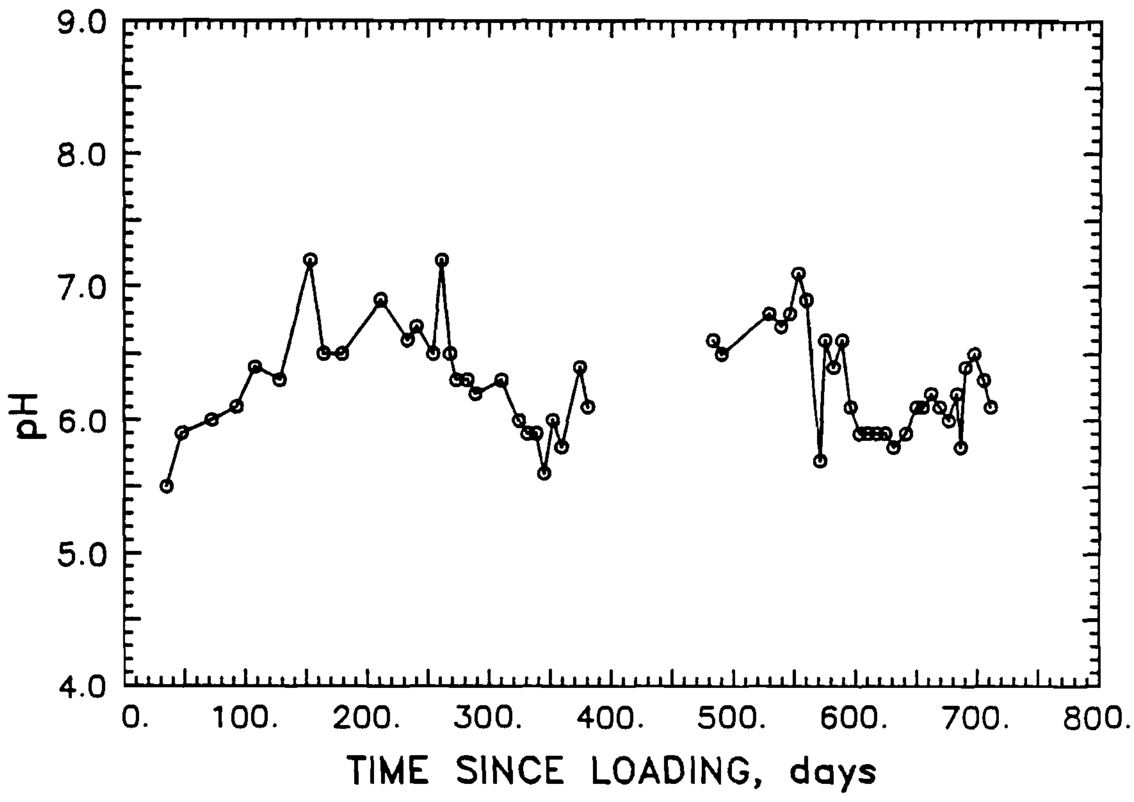


Figure 76. pH of Column 4 Leachate

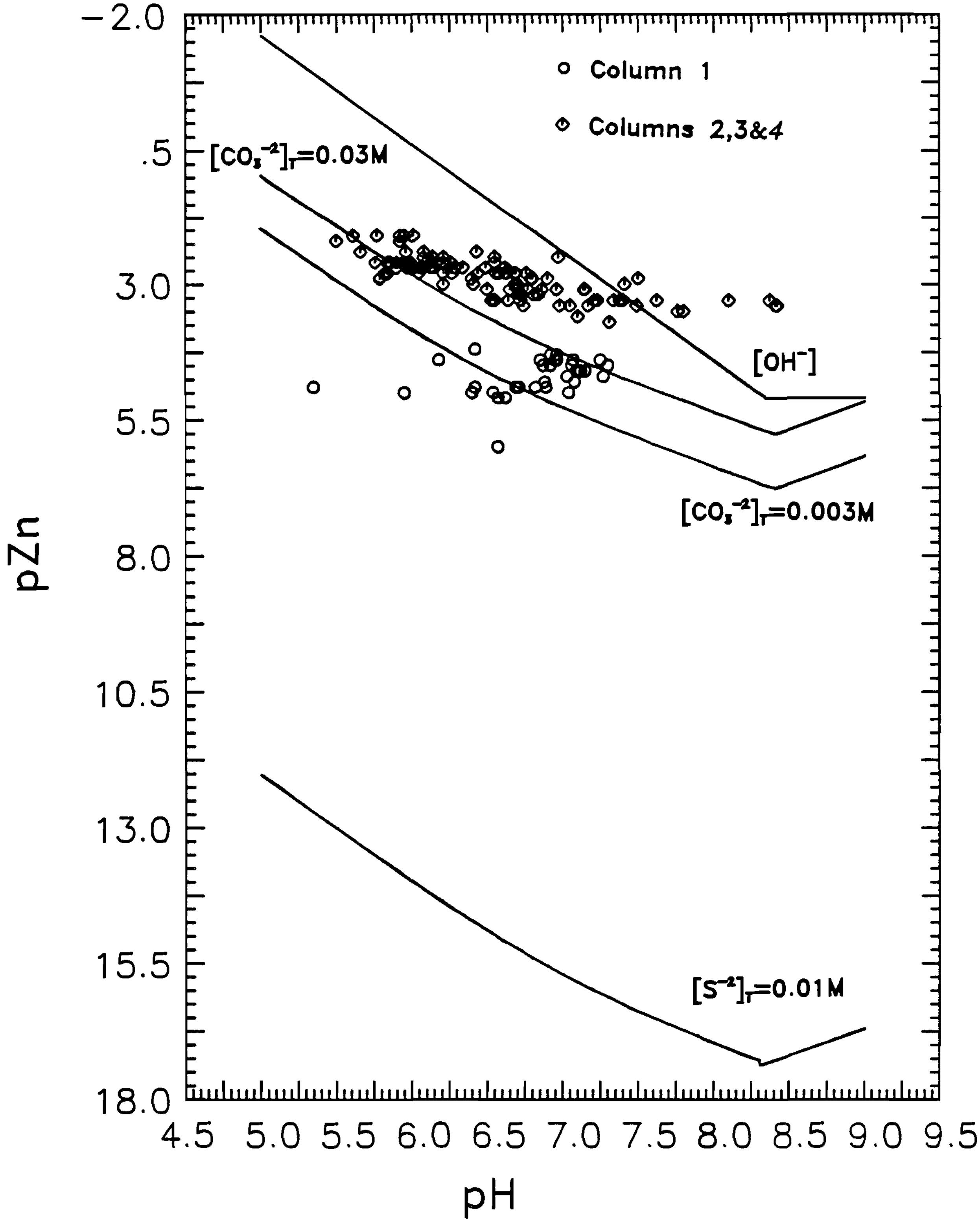


Figure 77. pH-pC Diagram for Zinc Solubility Under Carbonate, Hydroxide and Sulfide Control

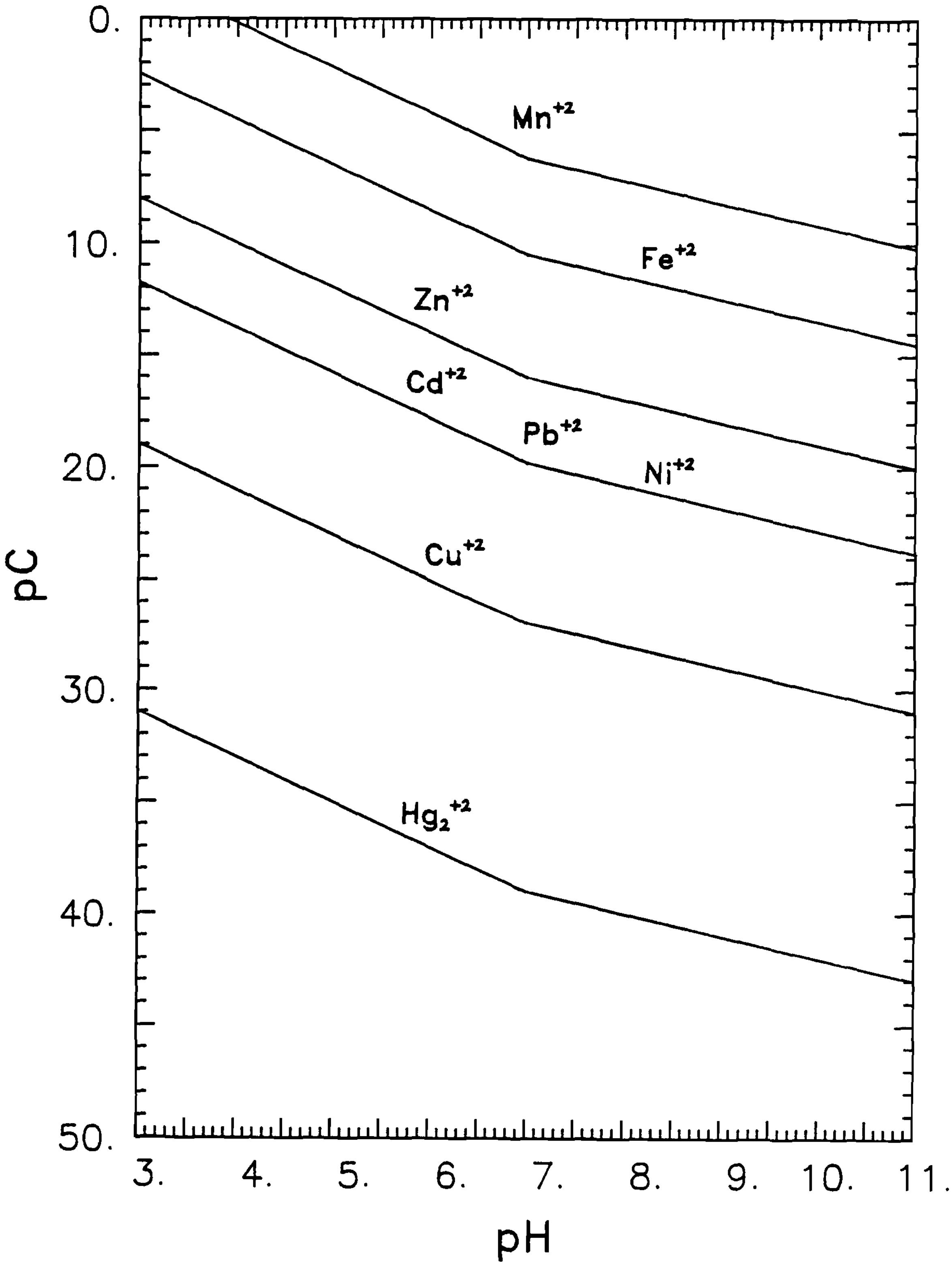


Figure 78. Solubility of Several Heavy Metals Under Sulfide Control (Sulfide C_t = 0.02 M)

if at all, and would, therefore, be most mobile under the indicated conditions. However, even at equilibrium concentrations of dissolved sulfide as low as 10^{-8} molar, the control of solubility of such metals as Hg_2^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2} and Ni^{+2} will remain in the domain of the sulfide system.

Ionic Strength and Activity--

To the extent that they represent relationships among reactants in media at infinite dilution, classical equilibrium constants actually will be in error with respect to conditions present in real aqueous systems. This error will be sufficiently slight and may be neglected in most fresh waters and many wastewaters. However, in systems containing high concentrations of dissolved solids, corrections due to ionic strength cannot be neglected. An examination of the composition of leachates as determined both in numerous prior studies and in the present work indicates that activity corrections arising from the high ionic strengths in the leachates may be substantial.

In the present studies, ionic strength was estimated on the basis of the empirical linear approximation developed by Langlier (1963), Russell (1970) and Lind (1976), or:

$$M = 1.6 \text{ X } 10^{-5} \text{ X Conductivity in } \mu\text{mho} \qquad \ldots(7)$$

The values of the conductivity and the ionic strength determined with Equation 7 as a function of time are presented in Figures 79 and 80. Since no systematic differences were observed in the values for Columns 2, 3 and 4, these data were averaged prior to plotting. However, the data for Column 1 were sufficiently distinct to justify a separate plot.

Examination of the data presented in Figure 79 indicates that the conductivities of the leachate from the sludge-laden columns were consistently higher than those of the control column and reflected the impact on leachate quality imposed by the inorganic ions leached from the sludge. It is also significant that the differences in conductivity between the control and sludge-laden columns appeared to be decreasing and began overlapping later in the study. This suggests that either the leachable components of the sludge were nearing exhaustion or that some mechanism such as sludge encapsulation was acting to dampen their availability. Indeed, visual examination of sludge particles randomly removed from the sludge-laden columns after the experimental period, conducted under low power (10 X) magnification, indicated a very obvious and uniform blackening of these particles, thereby suggesting a surface coating or encapsulation with sulfide deposits mixed possibly with carbonates.

These temporal trends of conductivity/ionic strength are clearly related to the initial composition of the wastes placed in the respective columns. As presented in Figure 80, the first 200 days of operation in the control column were characterized by a smooth and rapid decrease in ionic strength with a decrease of about 70 percent from initial levels. While simple washout of mobile conservative ions such as chloride and sodium was a major contributor to this decrease, biological conversion of such potentially ionic species as

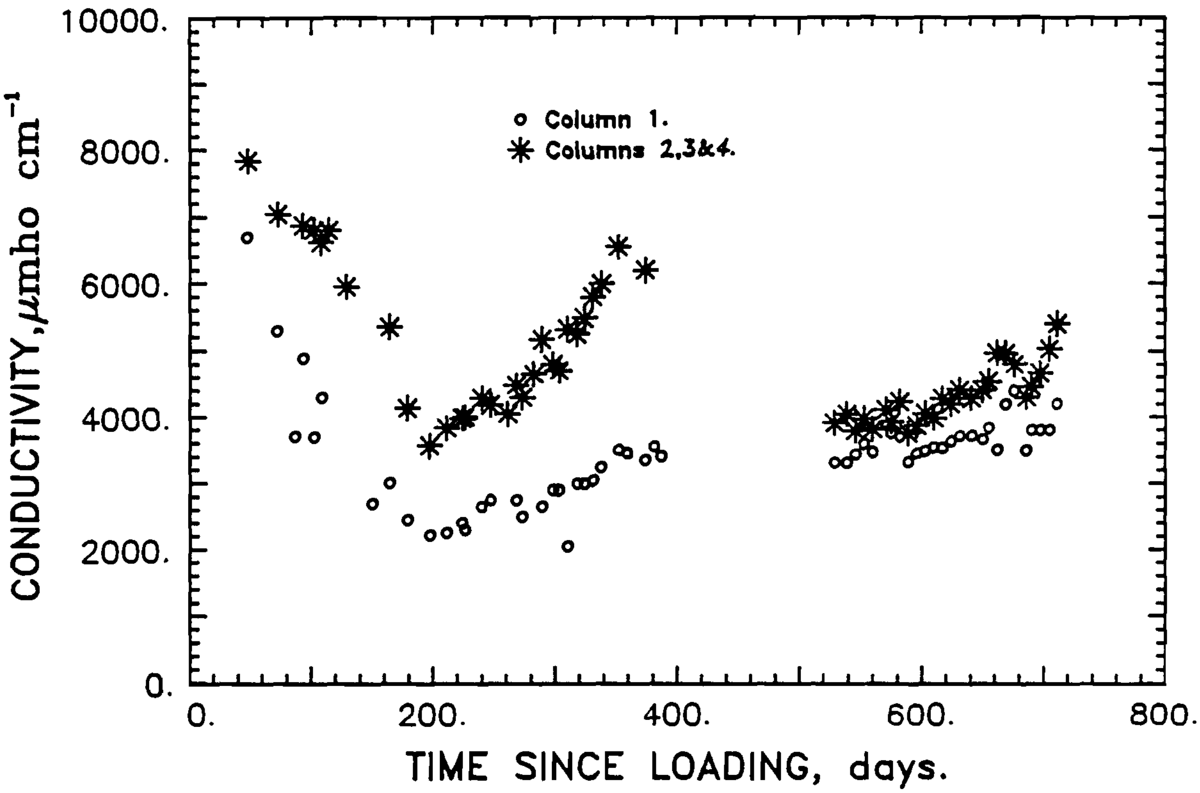


Figure 79. Conductivity as a Function of Time

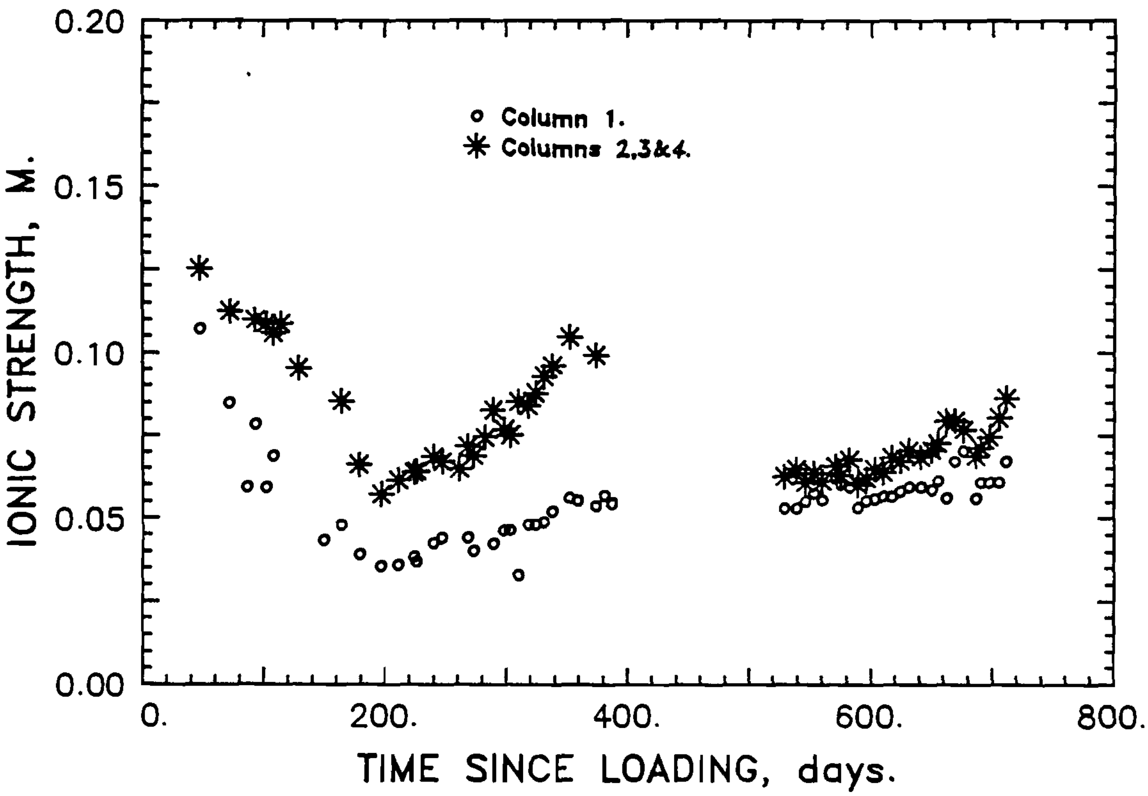


Figure 80. Ionic Strength as a Function of Time

sulfate and organic acids was also considered to be important to the reduction in ionic strength. Leachate from the metal sludge-bearing columns generally changed in a similar fashion except that a distinct pause was noted in the decrease of ionic strength between 50 and 150 days. This pause has been ascribed to a period during which heavy metal inhibition was limiting the biologically mediated reduction in ionic strength. It should also be emphasized that the resumption of the rapid decrease in ionic strength for Columns 2 through 4 corresponded closely to the reduction in leachate zinc (Figure 18), a measurable and reliable tracer of heavy metal contamination in the leachate, to levels below about 50 mg/L. This tended to support the premise that biological activity significantly influenced decreases in ionic strength during the early stages of the investigations.

Following the initial decrease in ionic strength, a substantial increase was observed during the 200 to 400-day period for both the control and the metal sludge-containing columns. The leachate from the metal sludge-containing columns recovered almost 70 percent of the initial decrease, while the recovery for the control column was only about 30 percent of the initial decrease in ionic strength. This increase in ionic strength was considered dependent on a corresponding pH increase with its attendant ionization of organic acids. The elevated volatile acid levels in the leachate from Columns 2 through 4 yielded a greater concentration of anions in response to a pH increase than observed for the control column (Figure 58). This accumulation of volatile acids was again attributed to inhibition of their biological conversation to methane caused by the excessive concentrations of heavy metals in the leachate from Columns 2 through 4 during this period, while the available alkalinity associated with the sludge served as an alkaline buffer pool to raise the pH.

Ionic strength data computed for the period between the resumption of leachate generation on Day 529 and termination of sampling at Day 711 show some overlap between the control column and those of the metal sludge-containing columns. A gradual increase, amounting to about 25 percent of the initial value, was observed for all columns during this period despite a relatively constant pH. These analytical data tend to reflect the effects of evaporation and attendant concentration of leachate constituents and corresponding conductivity and ionic strength for this stage of the investigations. In addition, physical encapsulation of the heavy metal sludge by deposits of sparingly soluble salts such as carbonates or sulfides may have acted to reduce the further availability of ionic species from the sludges in Columns 2 through 4.

To underscore the importance of changes in leachate ionic strength, activity coefficients have been computed for mono-, di- and trivalent ions as a function of time and are presented in Figure 81, again consolidating data for Columns 2, 3 and 4. The activity coefficients indicated in this figure were calculated by means of the Davies equation (Stumm and Morgan, 1970), or:

$$-\log \Upsilon = \frac{0.5\ Z^2 \mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.2\ \mu \qquad \ldots(8)$$

where; Z is the charge on the ion being considered, μ is the ionic strength, and Υ is the activity coefficient.

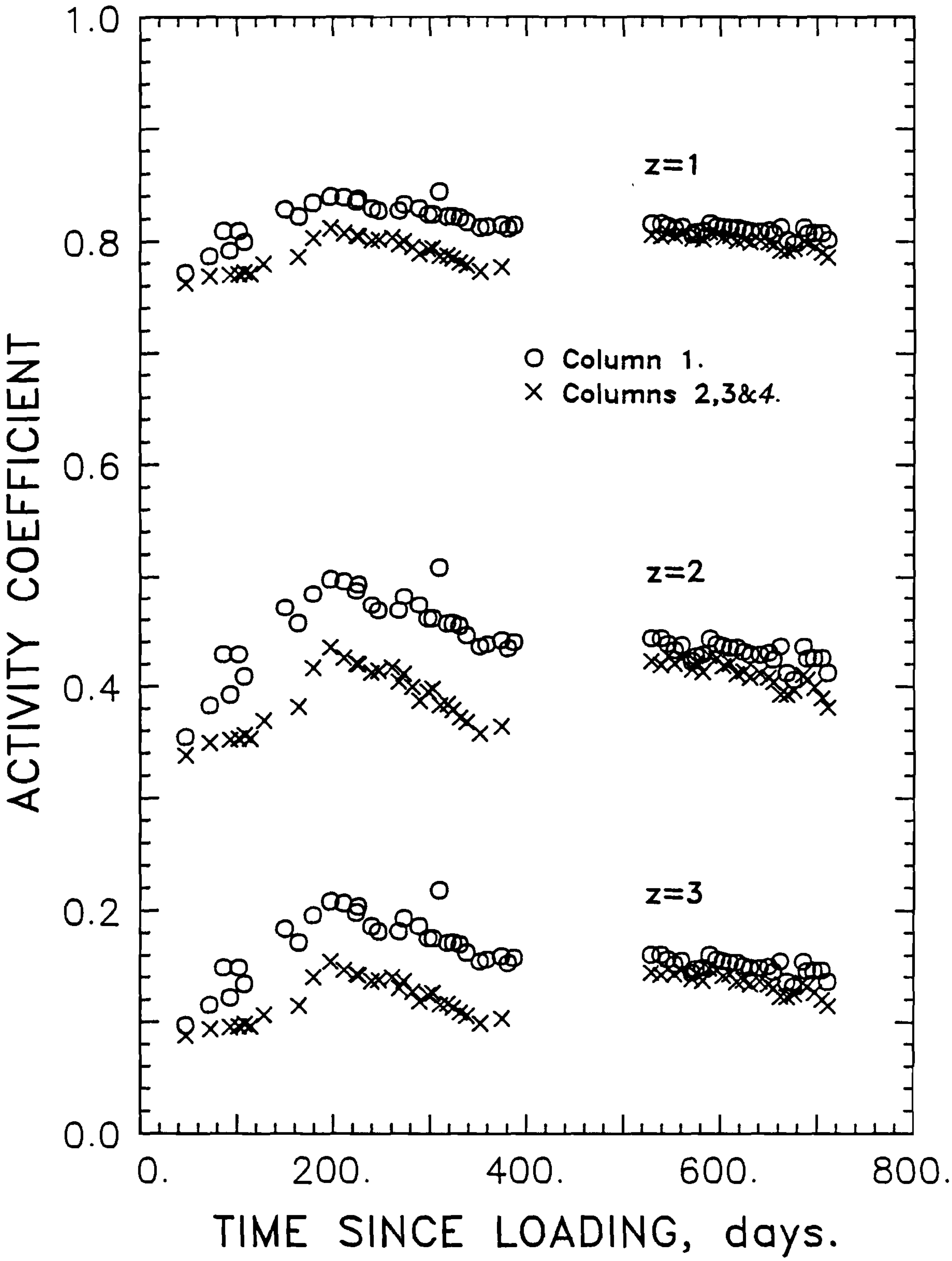


Figure 81. Activity Coefficients as a Function of Time

Although the activity coefficients presented seem significant especially in the case of trivalent ions, it is useful to examine a typical example to assess the actual impact of ionic strength on the nature of chemical processes in the leachate environment. The following example has been chosen to illustrate the impact of activity corrections on typical equilibria. Calcium is subjected to precipitation by phosphate as hydroxyapatiteand by carbonate as calcium carbonate, or

$$CaCO_3(s) \rightleftarrows Ca^{+2} + CO_3^{-2} \qquad \ldots(9)$$

$$Ca_{10}(PO_4)_6(OH)_2(s) \rightleftarrows 10Ca^{+2} + 6\ PO_4^{-3} + 2OH^- \qquad \ldots(10)$$

Given the data presented in Table 24, which are reasonably representative of column conditions, the significant equilibrium constants were corrected for activity (Table 25) and the calcium solubility profiles plotted for both the corrected and uncorrected cases (Figure 82). Perhaps the most striking aspect of these calculations is the relatively small impact of the activity corrections on the behavior of calcium phosphate and calcium carbonate interactions. Thus, calcium solubility will be under phosphate control over the full pH range regardless of activity corrections. Similar results have been obtained for other pertinent reactions (Pohland, et al., 1981).

These calculations indicate that, while the high ionic strength characteristic of landfill leachates will tend to impose moderate to large activity corrections on individual ionic species, the net impact will generally be so obscured by the chemical complexity of the landfill environ-ment and by analytical uncertainties as to be virtually undetectable. However, considering the magnitude of calculated activity coefficients (Figure 81), it is important that this factor be examined carefully in any case where its impact may be in doubt.

Oxidation-Reduction Potential--

The oxidation-reduction potential prevailing within the landfill environment will play an important role in determining speciation of several leachate constituents. Thus, several potentially significant metals will undergo redox-dependent transformations which will strongly influence their mobility and potential for migration through and from the landfill site. Included are such metals as $Mn(VII)/MnO_2/Mn^{+2}$, Fe^{+3}/Fe^{+2}, $Cr(VI)/Cr^{+3}/Cr^{+2}$ and Hg^{+2}/Hg_2^{+2}. In addition, and of similar significance, is the availability of $SO_4^{-2}/S(s)/S^{-2}$, since the production of sulfide under reducing conditions has classically been regarded as the major mechanism controlling metal mobility in landfill leachates due to the precipitation of very sparingly soluble metal sulfides. The dominance of this mode of metal fixation in landfills is further highlighted by the E_c-pH diagram (Figure 83) for this redox system.

The variation of sulfide levels with respect to time are shown in Figures 84 through 87, while the average values of these levels are presented in Figure 88. These data indicate that, although sulfide analyses were somewhat erractic, sulfide was available in excess to enter into the aforementioned reactions throughout the experimental period.

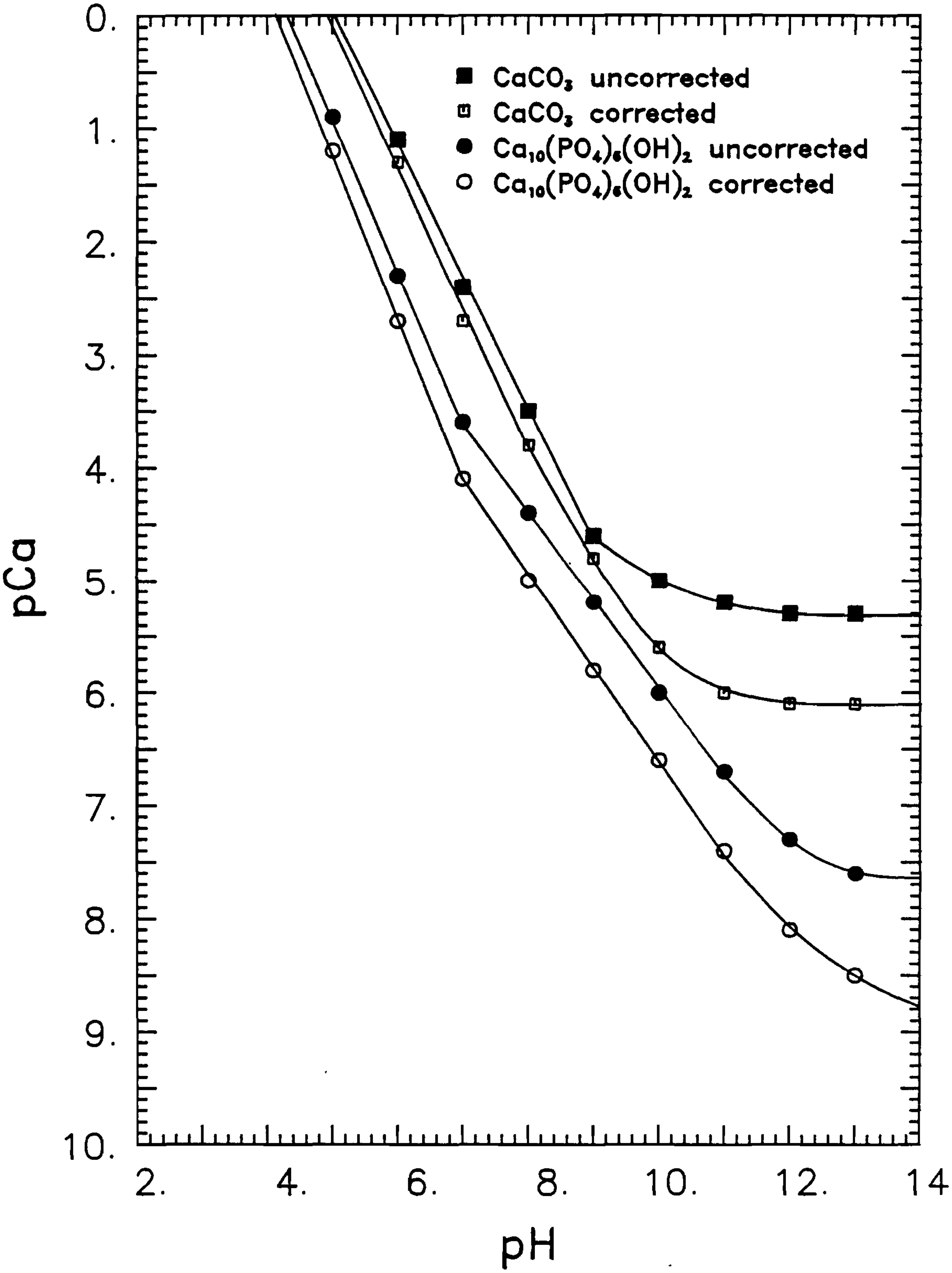


Figure 82. Solubility Diagrams for Calcite and Hydroxyapatite With and Without Activity Corrections

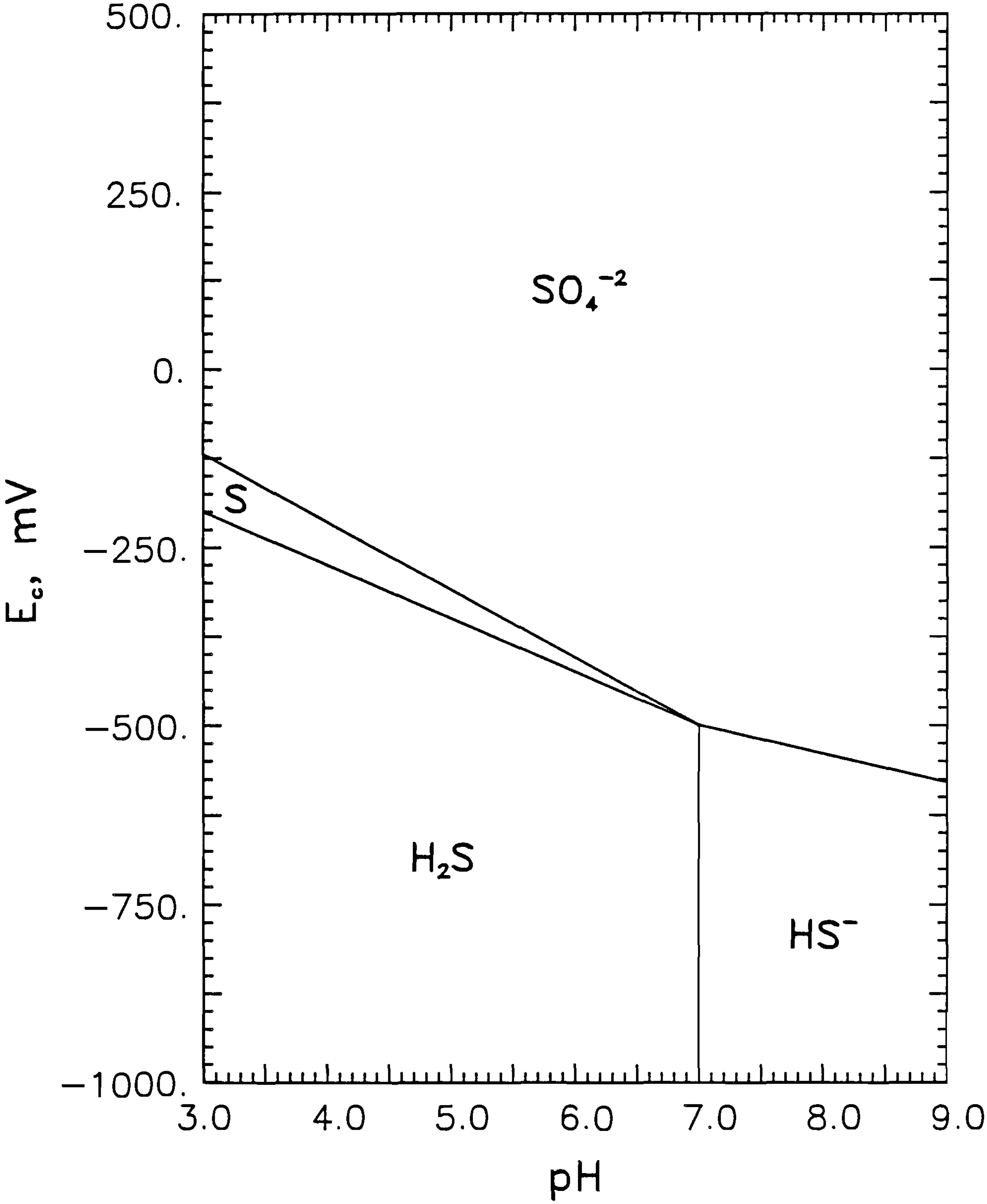


Figure 83. E_c-pH Diagram for the $SO_4^{-2}/S^o/S^{-2}$ System

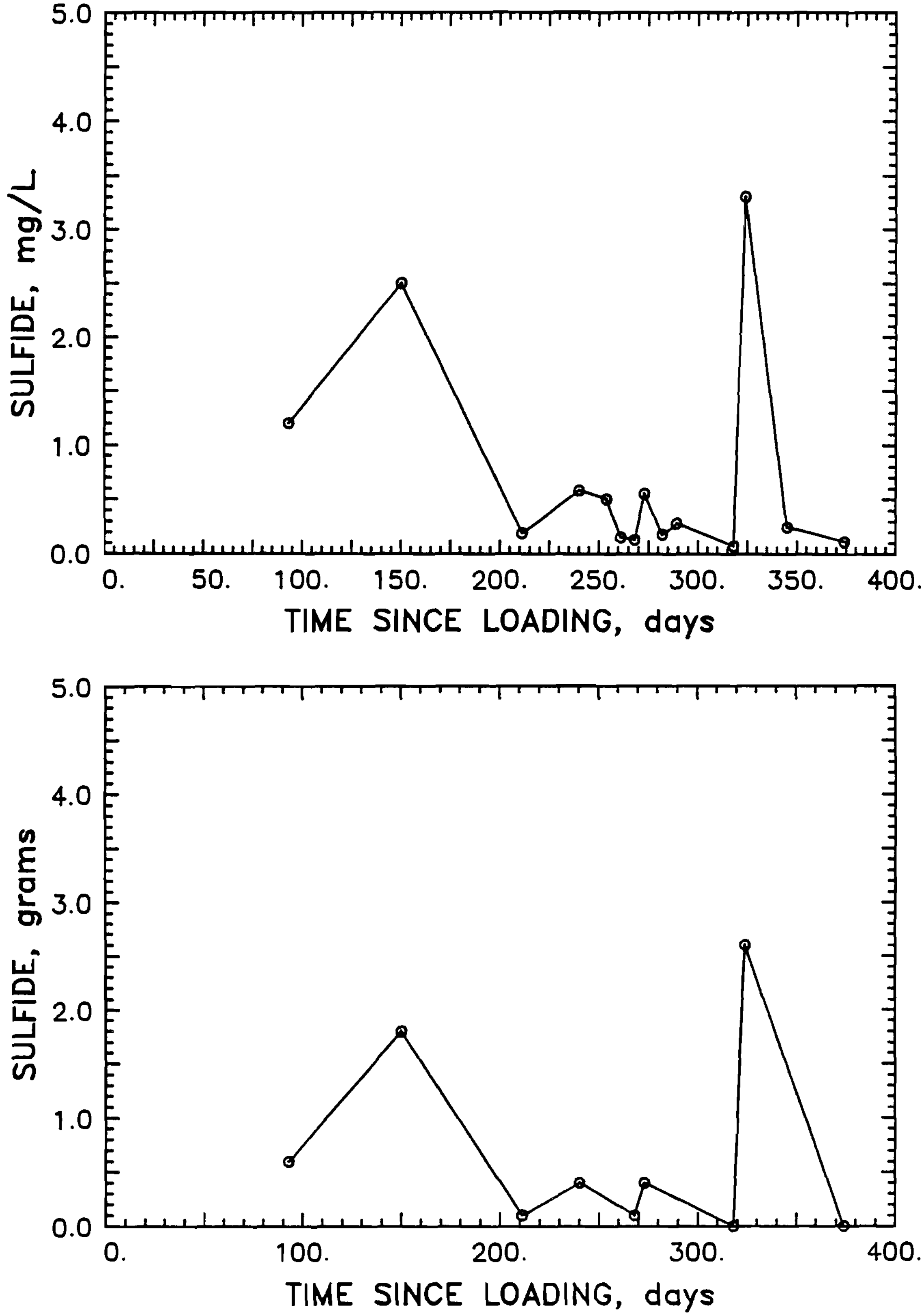
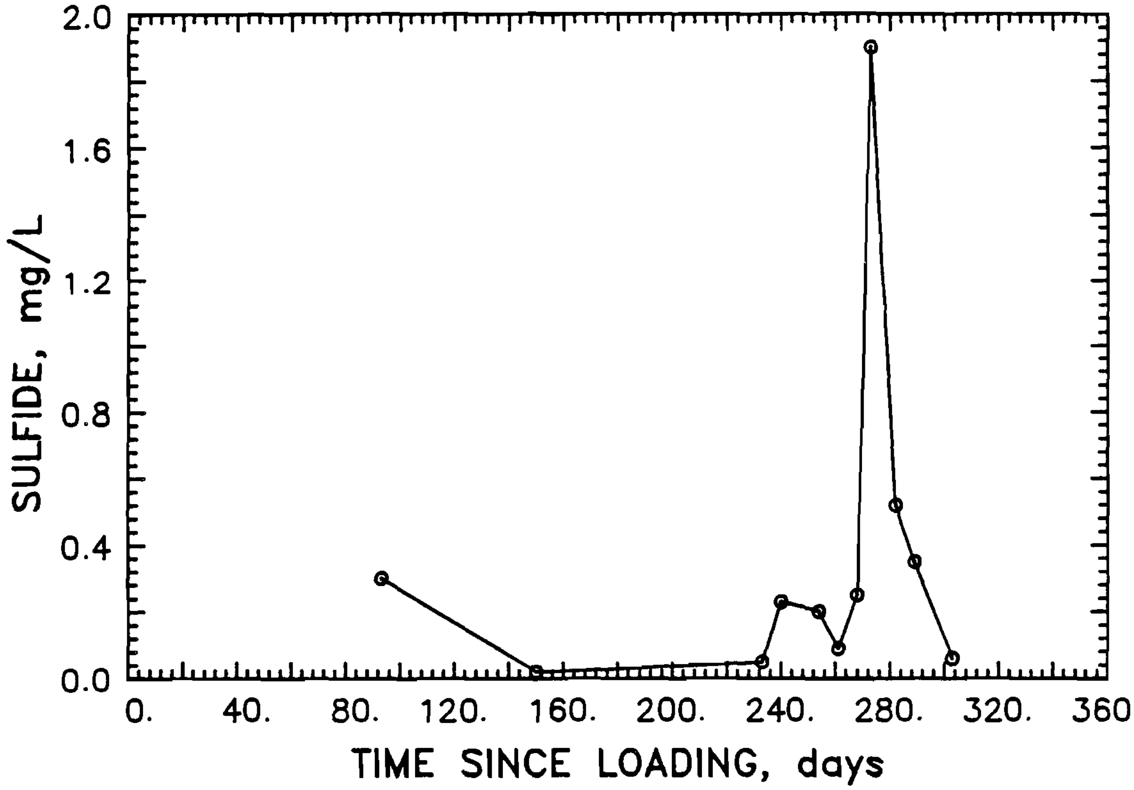


Figure 84. Sulfide Content of Column 1 Leachate



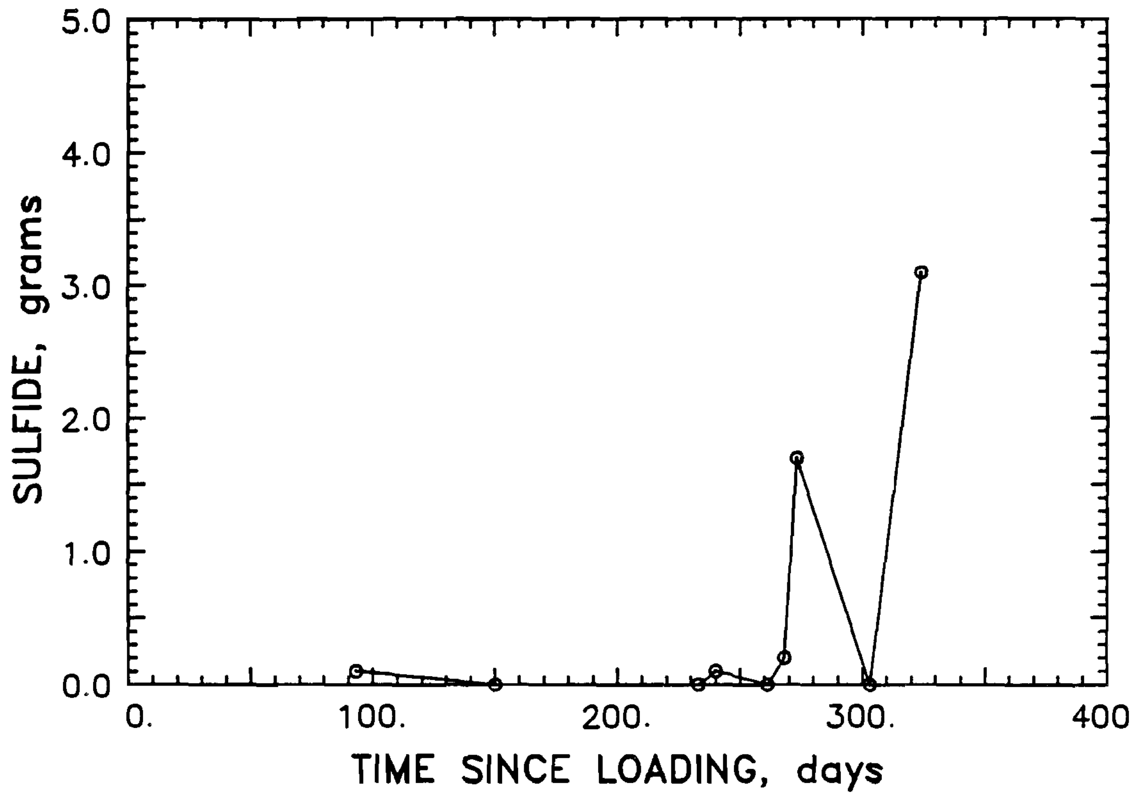


Figure 85. Sulfide Content of Column 2 Leachate

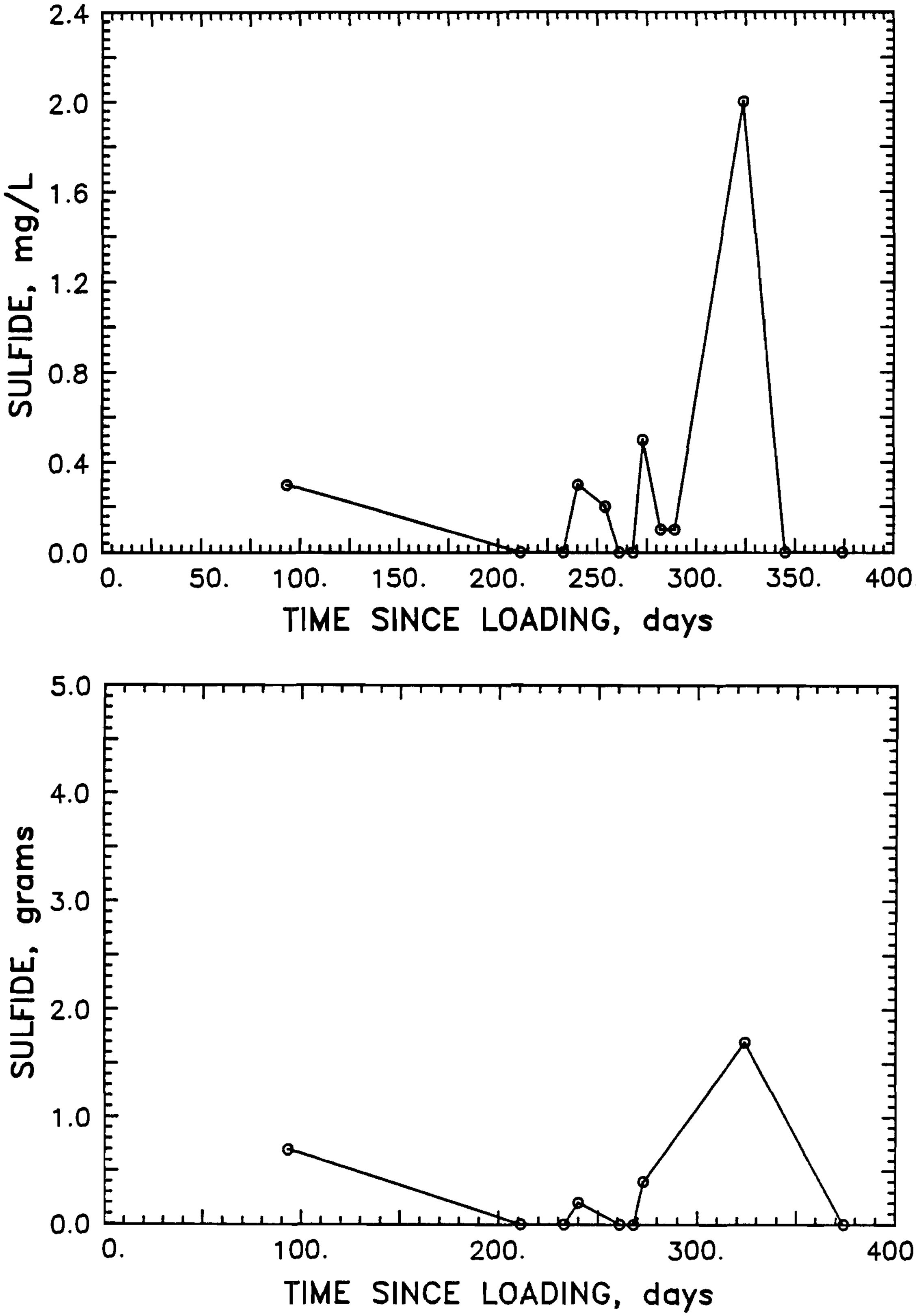


Figure 86. Sulfide Content of Column 3 Leachate

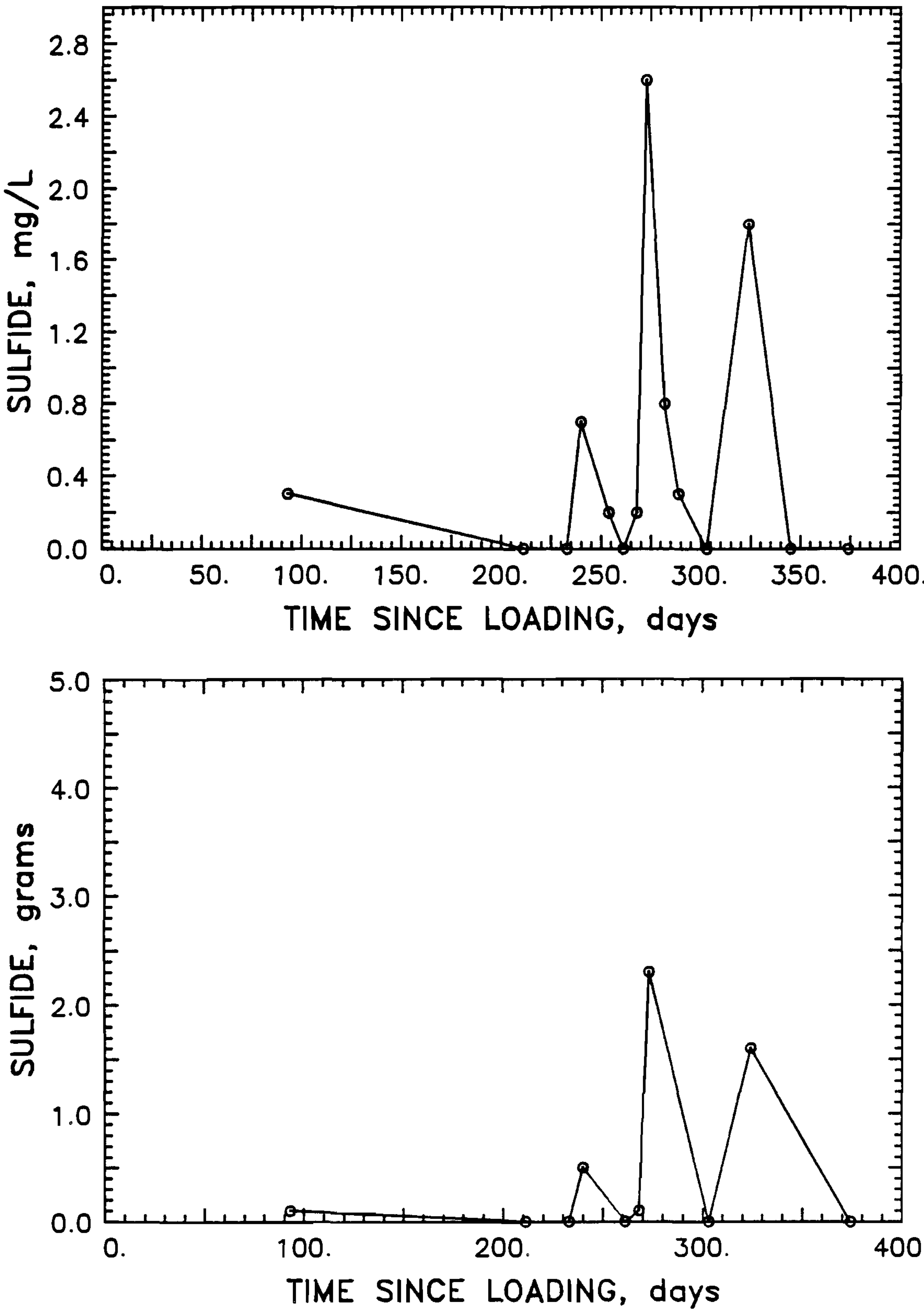


Figure 87. Sulfide Content of Column 4 Leachate

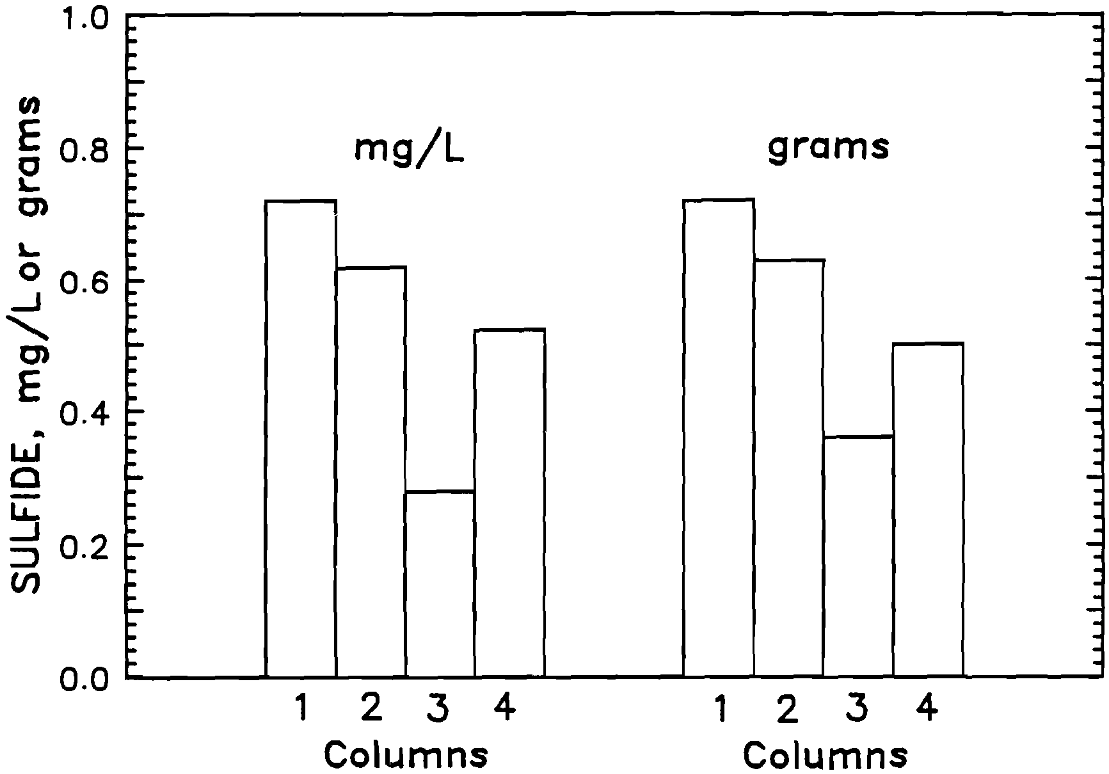


Figure 88. Average Content of Sulfide in the Leachates

TABLE 24. CONDITIONS CHOSEN FOR ACTIVITY EFFECT CALCULATIONS

Parameter	Value Used
$[CO_3]_T$	5.5×10^{-3} M
$[PO_4]_T$	1×10^{-4} M
Activity Coefficients	
γ_1 (Z=1)	0.78
γ_2 (Z=2)	0.38
γ_3 (Z=3)	0.11

TABLE 25. UNCORRECTED AND (CORRECTED) EQUILIBRIUM CONSTANTS

Symbol	Reaction	pK
K_{so} (HA)	Solubility of Hydroxyapatite	112.0 (101.8)
K_{so} (CA)	Solubility of Calcium Carbonate	8.4 (7.6)
K_{a1} (H_2CO_3)	Dissociation Constants	6.4 (6.2)
K_{a2} (H_2CO_3)	of Carbonic Acid	10.4 (10.0)
K_{a2} (H_3PO_4)	Dissociation Constants	7.2 (6.8)
K_{a3} (H_3PO_4)	of Phosphoric Acid	12.3 (11.7)

Aromatic Hydroxly as a Mobilizing Ligand--

As indicated previously, the role of complexation in complicated matrices such as leachates involves considerable uncertainty. Complexing agents, by converting sparingly soluble salts to soluble complexes, can counteract the impact of precipitant ions and thus increase the solubility of metals. Previously reported investigations have discounted significant complexation between even the most abundant inorganic ligands, such as chloride and sulfate, and any of the metals common to the metal sludges used in this research (Pohland, et al., 1982). Likewise, with one important exception, identified organic species, including carbohydrates and volatile acids, are simply too weak as ligands to be of substantial influence in heavy metal solubilization. The one exception is represented analytically in these studies by the aromatic hydroxyl (ArOH) compounds which provided a measure of the moderate to high molecular weight tannins and humic substances. Such compounds appear to be of pivotal importance in the control of the solubility of certain heavy metals.

Among the metals commonly regarded as heavy metals, routine monitoring was conducted during these studies for cadmium, chromium, copper, iron, manganese, nickel and zinc. Due in part to the composition of the admixed heavy metal sludges and to the general solubility behavior of these metals, the only elements detected with any consistency in the leachates which originated primarily from the metal sludge were cadmium, nickel and zinc. Moreover, since zinc was the major heavy metal in the admixed sludge (Table 6) and attained the highest concentrations of any of the heavy metals in the leachates, an initial examination of the solubility behavior of this element provided significant direction regarding solubility control in landfill leachates.

As discussed previously (Figure 77), the major potential solubility control for zinc is associated with sulfide as the precipitant, with carbonate providing the next most effective precipitant, and hydroxide being the least likely to form solid zinc species in these leachates. By plotting the measured pZn versus pH values from these studies also on Figure 77, certain observations emerge. First, the three metal sludge-laden columns showed little difference in the pZn-pH values. Hence, all three of these columns were at apparent saturation in terms of zinc and the leachate environment; a probable consequence of the intimate contact and resulting more complete equilibration provided by recycle. Secondly, while these data tended to cluster mainly between the carbonate and hydroxide solubility curves, those at high pH exceeded the solubility limits of even hydroxide solubility control. Therefore, whatever solid phase was controlling zinc solubility, there was superimposed upon this system some factor which acted to increase solubility. The most logical explanation was the presence of some complexing agent.

As indicated previously, the most likely complexing agents in leachates are the moderate to high molecular weight phenolic compounds arising from the decomposition of plant materials and generally referred to as humic substances. The aromatic hydroxyl (ArOH) groups measured in the leachates from these studies provided an effective measure of these substances. As was demonstrated earlier, the ArOH levels were generally high during the initial phases of leachate generation in all four columns and then decreased rapidly to essentially constant levels (Figures 40 through 43). While this constant ArOH level was maintained in the leachate from the control column (Column 1) and from Column 2 during the subsequent period of the studies, a later increase in ArOH in the leachates of Columns 3 and 4 was noted. This again reflected the fluctuating nature of the inherent stabilization processes, i.e., a sequence of microbial inhibition followed by acclimation in the metal sludge-bearing columns.

The apparent relationship between ArOH and soluble zinc concentrations is evidenced by the plot of Zn versus ArOH presented in Figure 89. A marked positive correlation between aromatic hydroxyl and zinc solubility strongly supports the concept that humic substances, as quantified by the aromatic hydroxyl analysis, played a major role in zinc solubility in these leachates. This observation is in reasonable concurrence with the estimate by Reuter (1977) of +20 for the log of the formation constant of many heavy metal-humic acid complexes. Large positive values of the formation constant indicates a strong metal mobilizing potential for these ligands.

Based on the promising results with zinc, similar plots for cadmium and nickel versus ArOH were prepared and are presented in Figures 90 and 91. Although these data are more scattered than in the case for zinc, the positive correlation between the respective metals and ArOH is again obvious. This led to the ultimate conclusion that the behavior of most of the heavy metals during landfill stabilization is largely reflected in leachate concentrations tempered by the compensating influences of precipitation and complexation. Precipitation and filtration in the waste matrix tends to capture and store the heavy metals, whereas humic-like substance interaction leads toward mobilization but perhaps also a reduction in toxicity effects over the non-complexed species.

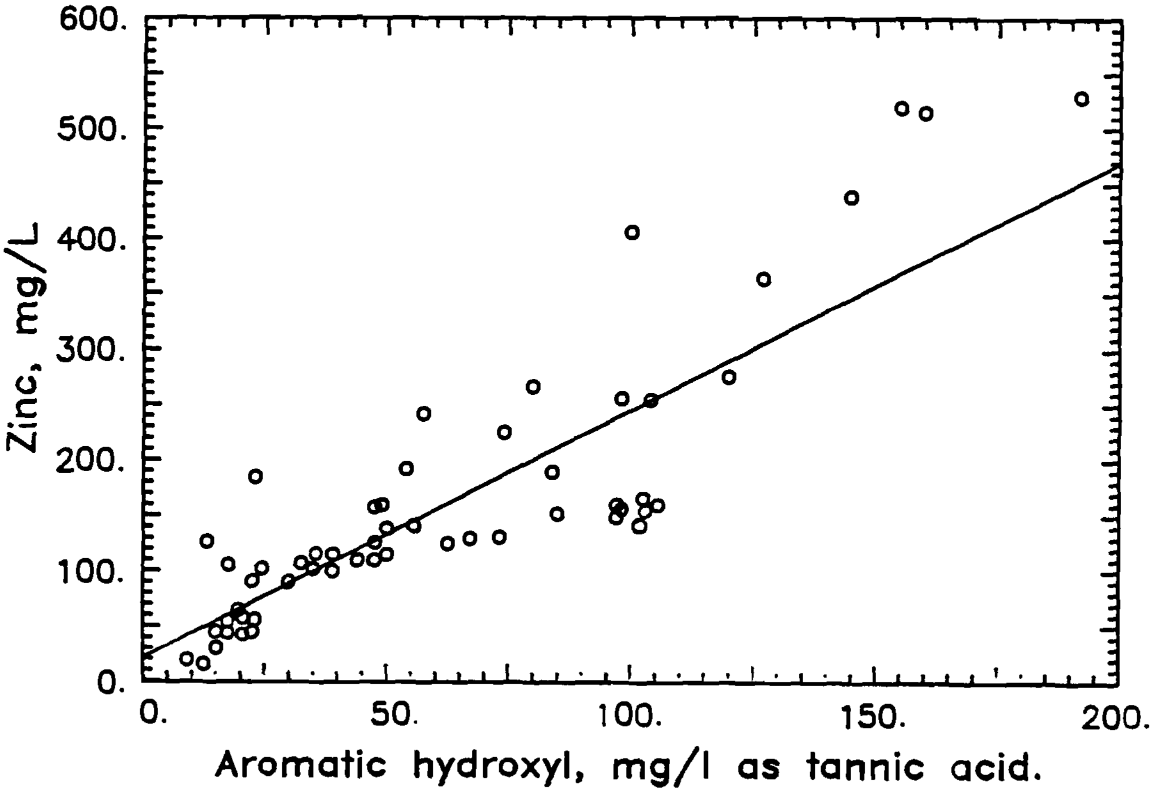


Figure 89. Zinc Concentration Versus Aromatic Hydroxyl Concentration

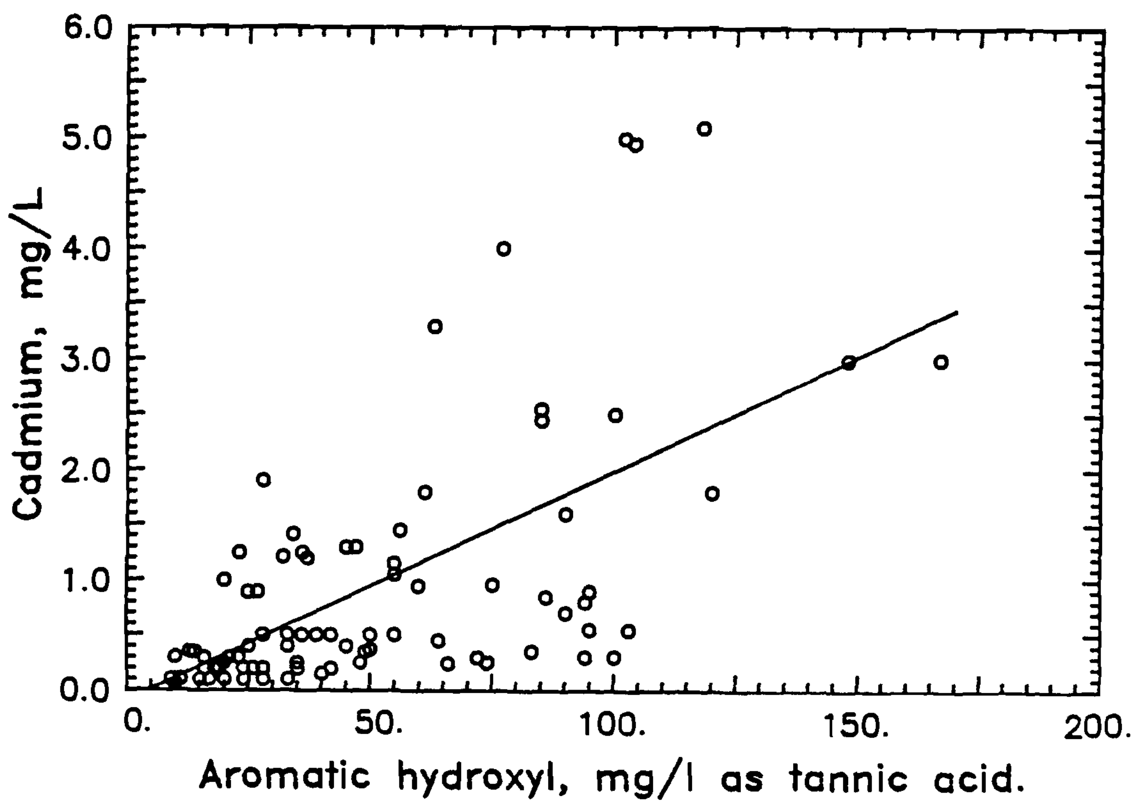


Figure 90. Cadmium Concentration Versus Aromatic Hydroxyl Concentration

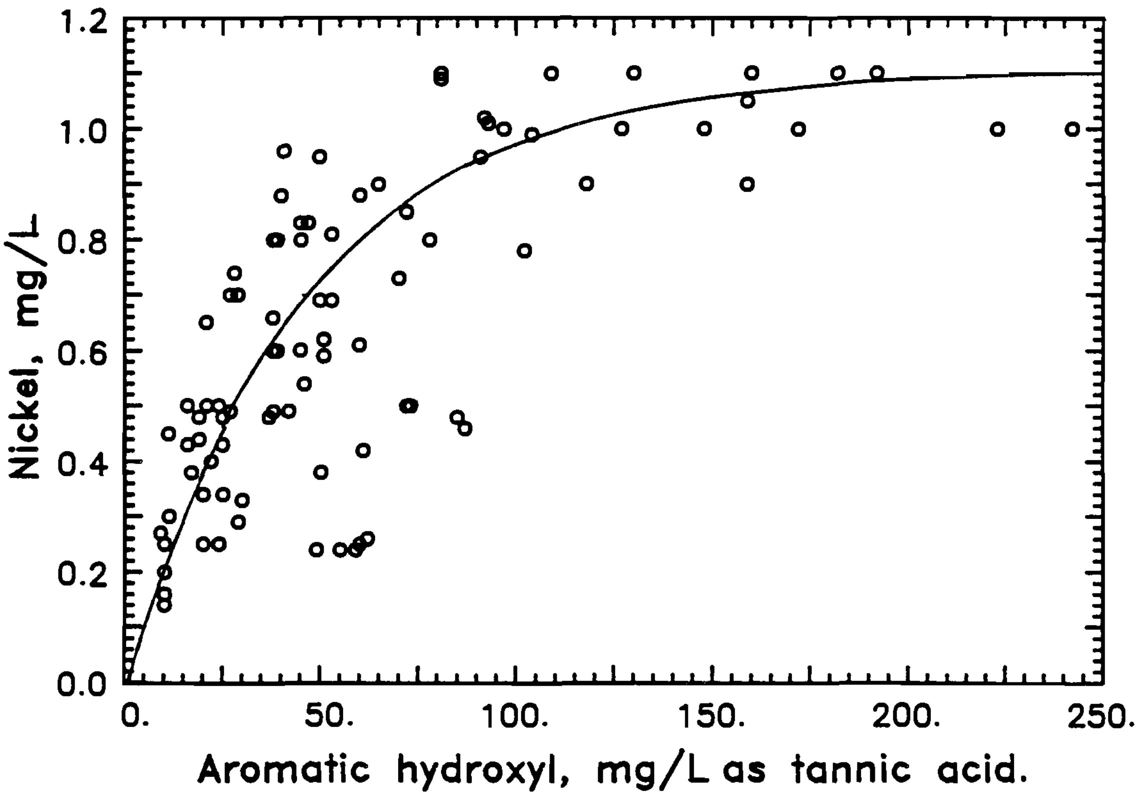


Figure 91. Nickel Concentration Versus Aromatic Hydroxyl Concentration

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APPENDIX A

SPECIAL ANALYTICAL METHODS

TABLE A-1. PROCEDURE FOR ACID DIGESTION OF METAL PLATING WASTE TREATMENT SLUDGE PRIOR TO METAL AND SULFATE ANALYSIS

1. Obtain approximately 1 gram of sample and determine its exact weight;
2. Place each sample in a 250 mL beaker with 100 mL distilled water and 10 mL concentrated nitric acid;
3. Cover with a watch glass and boil gently to near dryness (less than 25 mL);
4. Add 10 mL concentrated nitric acid and again boil to near dryness;
5. Add 10 mL 30% hydrogen peroxide and boil until effervescence subsides; and,
6. Cool and dilute to 100 mL.

TABLE A-2. REAGENTS AND PROCEDURE FOR DETERMINATION OF AROMATIC HYDROXYL

Reagents:

1. Tannin-Lignin Reagent: Add 100 g Sodium Tungstate ($Na_2WO_4.2H_2O$) and 25 g Sodium Molybdate ($Na_2MO_4.2H_2O$) to 700 mL distilled water Add 50 mL 85% Phosphoric Acid (H_3PO_4) and 100 mL concentrated Hydrochloric Acid (HCl) and reflux gently for 10 hours. Add 150 g Lithium Sulfate (Li_2SO_4), 50 mL distilled water, and a few drops liquid bromine. Boil without condenser for 15 minutes to remove excess bromine, cool to 25^{o}C, dilute to 100 mL, and filter. Store tightly stoppered in a ground glass reagent bottle. Discard if reagent turns green.

2. Carbonate-Tartrate Reagent: Dissolve 200 g Sodium Carbonate (Na_2CO_3) and 12 g Sodium Tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$) in 750 mL hot distilled water, cool to 25^{o}C, and dilute to 100 mL.

3. Stock Tannic Acid solution, 1000 mg/L: Dissolve 1.000 g Tannic Acid in distilled water, dilute to 1000 mL. This solution can be stored from 4-6 weeks at 4^{o}C. Discard at first signs of growth or change in absorption spectra.

4. Standard Tannic Acid Solutions: Prepare daily dilutions ranging from 1 - 10 mg/L of Tannic Acid.

Procedure:

1. In duplicate, add 50 mL of sample to reaction vessel.

2. Add in rapid succession 1 mL tannin-lignin reagent and 10 mL carbonate-tartrate reagent.

3. Mix well, and let stand for 30 minutes.

4. Measure absorbance at the wavelength maxima determined for the standard solution (600-700 nm).

5. Repeat with appropriate reagent and sample blanks.

TABLE A-3. REAGENTS AND PROCEDURE FOR DETERMINATION OF COMPOUNDS CONTAINING CARBOXYL GROUPS

Reagents:

1. Sulfuric Acid, diluted: Mix equal volumes of analytical grade Sulfuric Acid, sp. gr. 1.84, and distilled water.

2. Sodium Hydroxide, 4.5 M: Dissolve 180 g of Sodium Hydroxide in distilled water and dilute to 1000 mL.

3. Hydroxylamine Sulfate, 10%: Dissolve 10 g Hydroxylamine Sulfate in 100 mL distilled water.

4. Acidic Ethylene Glycol Reagent: Mix 30 mL Ethylene Glycol with 4 mL diluted Sulfuric Acid. Prepare fresh daily.

5. Hydroxylamine Reagent: Mix 20 mL 4.5 NaOH and 5 mL 10% Hydroxylamine Sulfate. Prepare fresh daily.

6. Acidic Ferric Chloride Reagent: Dissolve 20 g Ferric Chloride in 500 mL distilled water, add 20 mL concentrated Sulfuric Acid and dilute to 1000 mL.

7. Stock Acetic Acid Solution, 10 g/L: Dilute 10 mL concentrated Acetic Acid to 1000 mL with distilled water. Can be stored at 4°C for not more than 72 hours or when absorbance spectra changes.

8. Standard Acetic Solutions. Prepare dilutions of stock acetic acid solution ranging from 0.5 to 10 g/L.

Procedure:

1. Place 1 mL of sample in a 25 mL volumetric flask.

2. Add 1.7 mL acidic ethylene glycol reagent.

3. Place in boiling water bath for 3 minutes.

4. Cool in water bath for 2 minutes.

5. Add 2.5 mL hydroxylamine reagent.

6. Add 10 mL ferric chloride reagent.

7. Fill to volume and let stand for 5 minutes.

8. Measure absorbance at 500 nm.

9. Repeat for appropriate reagent and sample blanks.

TABLE A-4. PROCEDURE FOR DIGESTION OF LEACHATE SAMPLES PRIOR TO METAL ANALYSIS

Procedure:

1. Place 100 mL of sample in a 250 mL beaker.

2. Add 10 mL concentrated nitric acid.

3. Cover with a watch glass and boil gently to near dryness.

4. Add 10 mL concentrated nitric acid and boil to near dryness.

5. Add 5 ml 30% hydrogen peroxide and boil until effervescence subsides.

6. Cool and dilute to 25 mL.

TABLE A-5. SAMPLE COMPUTATION OF LEACHATE VOLUME AND COMPONENT MASS

$$V_t = \frac{Cl_o V_o - \sum_{t=1}^{n} Cl_s V_s + \sum_{t=1}^{n} Cl_a V_a}{Cl_t}$$

Column No. 1

t = 197 days since loading columns

Cl_o = initial chloride concentration in leachate (623 mg/L)

V_o = initial volume of leachate in columns (560 liters)

$\sum_{t=1}^{n} Cl_s V_s$ = mass of chloride withdrawn during sampling (6010 mg)

$\sum_{t=1}^{n} Cl_a V_a$ = mass of chloride added during tap water addition (5250 mg)

Cl_t = measured chloride concentration at time = t (380 mg/L)

Thus,

$$V_t = \frac{623 \times 560 - 6010 + 5250}{380} = 96 \text{ liters at Day 197 in Column 1}$$

Then,

$$M_t = C_t \, V_t$$

where

M_t = mass of any component in Column at time = t

C_t = Concentration of that component in leachate at time = t